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USSR: Chemistry

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SCIENCE & TECHNOLOGY

USSR: CHEMISTRY

CONTENTS

ANALYTICAL CHEMISTRY

- Use of Microcolumn Chromatographs To Monitor Chemical Quality
(Vladislav Ksionzhik; *TEKHNIKA-MOLODEZHI*, No 6,
Jun 87)..... 1
- X-ray Fluorescent Assay of Rubidium in Sea Water
(V. A. Lebedev, U. V. Alvares, et al.; *VESTNIK
MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA*, No 2,
Mar-Apr 87)..... 9
- Metrological Aspects of Chemical Analysis
(L. N. Filimonov; *ZHURNAL ANALITICHESKOY KHIMII*, No 4,
Apr 87)..... 9
- Some Formalized Concepts and Quantitative Estimates in
Chemical Analysis Based on Computers
(L. A. Gribov, Yu. M. Luzhkov, et al.; *ZHURNAL
ANALITICHESKOY KHIMII*, No 4, Apr 87)..... 10

AEROSOLS

- Charge of Aerosol Particles in Inert Gases in Presence of
External Electric Field
(A. V. Zagnitko, A. A. Kirsh; *ZHURNAL FIZICHESKOY
KHIMII*, No 5, May 87)..... 11

ALKALOIDS

Synthetic Analogs of Peganin Alkaloids

- (M. V. Telezhenetskaya, A. L. Dyakonov; KHIMIYA
PRIRODNYKH SOYEDINENIY, No 2, Mar-Apr 87)..... 12

CATALYSIS

23 Phase Portraits of Simple Catalytic Oscillator

- (A. I. Khibnik, V. I. Bykov, et al.; ZHURNAL
FIZICHESKOY KHIMII, No 5, May 87)..... 13

Spatial Structures in Oscillating Reactions of Oxidizing Tetraazamacrocyclic Complexes of Nickel and Copper and Influence of Surface on Reactions

- (K. B. Yatsimirskiy, L. N. Zakrevskaya, et al.;
TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA, No 2,
Mar-Apr 87)..... 14

Nonstationary Catalytic Preparation of Sulfur in Klaus Process

- (Yu. Sh. Matros, A. N. Zagoruyko; DOKLADY AKADEMII NAUK
SSSR, No 6, Jun 87)..... 14

CHEMICAL INDUSTRY

UzSSR Chemists and Chemization Tasks

- (S. Yunusov, M. Askarov; PRAVDA VOSTOKA, 29 May 87).... 16

Air Pollution Reduction by Conversion of Plant Exhaust Sulfur Dioxide to Sulfuric Acid

- (R. Khadzhiyev; SOTSIALISTICHESKAYA INDUSTRIYA,
29 Apr 87)..... 20

COLLOID CHEMISTRY

Influence of Surface-Active Substances on Rheologic Properties of Dispersions of Calcium Carbonate in Organic Fluorine Media

- (Ye. V. Guseva, F. D. Ovcharenko; UKRAINSKIY
KHIMICHESKIY ZHURNAL, No 6, Jun 87)..... 21

PMR Testing of Water Content in Hydrated Inverted Aerosol Micelle Systems Containing Protein

- (N. L. Klyachko, A. V. Levashov, et al.; VESTNIK
MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA, No 3,
May-Jun 87)..... 22

Paramagnetic Hydrophilic Probing of Multilayer Liposomes of Cationic Lipid-Like Monomers by PMR Method

- (V. V. Yegorov, Yu. Ye. Shapiro, et al.; VESTNIK
MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA, No 2,
Mar-Apr 87)..... 22

| | |
|---|----|
| Structure of Shock Wave in Polymer Liquid With Gas Bubbles (Z. P. Shulman, S. P. Levitskiy; DOKLADY AKADEMII NAUK BSSR, No 4, Apr 87)..... | 23 |
| Magnetic Effects in Recombination of Radical Pairs in Reactions of Carbonyl Compounds With Phenols in Micelles: Influence of Radical Structure (P. P. Levin, V. A. Kuzmin; IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA, No 5, May 87)..... | 23 |
| Ordinary and Resonant Raman Spectra of Methyl- and Ethylsulfoviologen in Microheterogeneous Systems (L. M. Kachapina, V. V. Trokhimets; ZHURNAL FIZICHESKOY KHIMII, No 6, Jun 87)..... | 24 |
| Thermographic Study of Electrolytic Iron Powders of Varying Chemical Composition (A. G. Zhigotskiy, S. I. Radoshinskaya, et al.; UKRAINSKIY KHIMICHESKIY ZHURNAL, No 6, Jun 87)..... | 25 |
| Coprecipitation of Certain Microscopic Powders With Ni (V. V. Skrobot'skaya-Medyalene, et al.; TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B, No 2, Mar-Apr 87)..... | 25 |
| COMBUSTION, EXPLOSIVES | |
| Explosive Chemical Reactions of Metals With Oxides and Salts in Solids (N. S. Yenikolopyan, A. A. Mkhitarian, et al.; DOKLADY AKADEMII NAUK SSSR, No 4, Jun 87)..... | 27 |
| Kinetics of Explosive Chemical Reactions in Solids (N. S. Yenikolopyan, A. A. Khzardzhyan, et al.; DOKLADY AKADEMII NAUK SSSR, No 5, Jun 87)..... | 28 |
| Photo-heat Inflammation of Cl ₂ -F ₂ Gaseous Mixtures (A. P. Suyetinov, Yu. L. Moskvina; KHIMICHESKAYA FIZIKA, No 4, Apr 87)..... | 28 |
| Parameters of Focal-Pulsating Combustion of Nitroglycerin Powder (V. N. Marshakov; KHIMICHESKAYA FIZIKA, No 4, Apr 87)... | 29 |
| Inflammation of Fuel Films Behind Shock Waves (B. Ye. Gelfand, S. M. Frolov, et al.; KHIMICHESKAYA FIZIKA, No 5, May 87)..... | 29 |
| Asymptotic Theory of Stationary Combustion Wave (S. I. Khudyayev; KHIMICHESKAYA FIZIKA, No 5, May 87)... | 30 |
| Methyldinitramine Thermochemistry and Enthalpy of Formation of Methylnitramine Radical (Ye. A. Miroshnichenko, L. I. Korchatova, et al.; DOKLADY AKADEMII NAUK SSSR, No 2, Jul 87)..... | 31 |

ELECTROCHEMISTRY

| | |
|---|----|
| Thermally Stimulated Currents in Metal 1-Glass Ceramic Metal 2 Systems (V. A. Belyy, Yu. I. Voronezhnev, et al., DOKLADY AKADEMII NAUK SSSR, No 4, Jun 87)..... | 32 |
| Influence of Nature of Lipid and Viologen on Transmembrane Electron Transfer in Vesicular Photosystem: Electron Donor - Ru(bipy) ₃ ²⁺ - Viologen - Oxidizer (Ye. Ye. Yablonskaya, V. Ya. Shafirovich; IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA, No 5, May 87)..... | 33 |
| Nuclear Magnetic Resonance of ⁷ Li and ¹¹⁹ Sn in Double Oxides Li ₂ TiO ₃ and Li ₂ SnO ₃ (A. A. Vashman, I. S. Pronin, et al.; ZHURNAL NEORGANICHESKOY KHIMII, No 6, Jun 87)..... | 33 |
| Sealed Lead-Hydrogen Battery (B. I. Tsenter, N. Yu. Lyzlov; ELEKTROKHIMIYA, No 5, May 87)..... | 34 |
| Nonadaptive Nature of Influence of Nonaqueous Electrolyte Components on Electrochemical Behavior of Lithium Ye. M. Shembel', I. M. Maksyuta, et al.; ELEKTROKHIMIYA, No 5, May 87)..... | 35 |
| Rearrangements of Complex Compounds and Quinone on Surface of Modified Electrodes (A. S. Gudovichyus, V. I. Razumas, et al.; TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B, No 1, Jan-Feb 87)..... | 36 |

FERTILIZERS

| | |
|---|----|
| Estonian Superphosphate Fertilizer Production Problems (V. Tsion; SOTSIALISTICHESKAYA INDUSTRIYA, 12 Jun 87)... | 37 |
| Production of Granules Suitable for Encapsulation by Thin Polymer Films From Melts of Nitrogen-Containing Fertilizers With Magnesium-Iron Additive (A. L. Taran, A. V. Taran, et al.; KHIMICHESKAYA PRMYSHLENNOST, No 6, Jun 87)..... | 40 |
| Prospects for Use of Lime-Ammonium Nitrate and Selenium (E. Ye. Khavkin; KHIMIYA V SELSKOM KHOZYAYSTVE, No 6, Jun 87)..... | 41 |

INORGANIC COMPOUNDS

| | |
|--|----|
| Auger Electron Spectroscopy of Titanium Films on Diamond Surface (V. G. Aleshin, A. G. Gontar, et al.; POVERKHNOST: FIZIKA, KHIMIYA, MEKHANIKA, No 6, Jun 87)..... | 42 |
| Quadrupole Interactions in NMR Relaxation of KSbF_6 (S. G. Kozlova, Yu. G. Kriger, et al.; ZHURNAL STRUKTURNY KHIMII, No 2, Mar-Apr 87)..... | 42 |
| Mechanochemical Activation and Dimensional Effect in Dissociated Sublimation of Solids (V. A. Ilyin, V. I. Kolynina, et al.; ZHURNAL PRIKLADNOY KHIMII, No 5, May 87)..... | 43 |
| Magnetism of Mixed Rare Earth and Uranium Selenides of Composition $\text{Ln}_2\text{U}_2\text{Se}_7$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$) (D. G. Barakadze, V. I. Chechernikov, et al.; SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR, No 2, May 87)..... | 44 |
| Structural Impurities as Indicators of Growth Mechanism of Natural Diamond Crystals (G. K. Blinova; DOKLADY AKADEMII NAUK SSSR, No 4, Jun 87)..... | 44 |
| Dislocation-Field Mechanism of Post-Emission of Electrons and Positive Ions From the Fractured Surface of an LiF Single Crystal (A. G. Lipson, V. A. Kuznetsov, et al.; DOKLADY AKADEMII NAUK SSSR, No 5, Jun 87)..... | 45 |
| Information Content of Speeds of Sound in Single Crystals (Yu. M. Sokolskiy; ZHURNAL FIZICHESKOY KHIMII, No 5, May 87)..... | 46 |
| Effects of Pressure and Electric Fields on the Ferroelectric-Antiferroelectric Phase Boundary in $\text{Pb}(\text{TiZr})\text{O}_3$ Ceramics (I. N. Polandov, O. K. Gulish, et al.; VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA, No 3, May-Jun 87)..... | 46 |
| Specific Conductivity of Molten Salts $\text{Ca}_2\text{F}-\text{CaCl}_2$, $\text{SrF}_2-\text{SrCl}_2$, and $\text{BaF}_2-\text{BaCl}_2$ (B. M. Boronin, V. D. Prisyazhnyy, et al.; UKRAINSKIY KHIMICHESKIY ZHURNAL, No 6, Jun 87)..... | 47 |
| Calculation of Ion-Electron Conductance of Oxides (V. F. Zinchenko, G. A. Teterin, et al.; UKRAINSKIY KHIMICHESKIY ZHURNAL, No 6, Jun 87)..... | 48 |

| | |
|---|----|
| Influence of CuO and Ag ₂ O on Electrical Characteristics of Barium Vanadate Glasses (L. D. Bogomolova, M. N. Glasova, et al.; FIZIKA I KHIMIYA STEKLA, No 2, Mar-Apr 87)..... | 48 |
| Changes in NKVV Auger Spectra of ZrN, NbN and Mo ₂ N (Yu. M. Shulga, V. I. Rubtsov, et al.; POVERKHNOST: FIZIKA, KHIMIYA, MEKHANIKA, No 7, Jul 87)..... | 49 |
| Pyroelectric Effect on Image Formation of Ferroelectric Crystals in Scanning Electron Microscope (N. N. Dremova, A. I. Yerko, et al.; POVERKHNOST FIZIKA, KHIMIYA, MEKHANIKA, No 7, Jul 87)..... | 50 |
| Effects of Cerium on Iron-Containing K-Al-B Glass (G. N. Belozerskiy, A. V. Kalyamin, et al.; FIZIKA I KHIMIYA STEKLA, No 3, May-Jun 87)..... | 50 |
| Conditions of Magnetite Crystallization in Glass and Its Effect on Electrophysical Properties of Glass (V. V. Tavgen, Ye. V. Shpak, et al.; VYESTSI AKADEMII NAVUK BSSR: SERYYA KHMICHNYKH NAVUK, No 3, May-Jun 87)..... | 51 |
| Thermal Stability of Alkali-Metal Hexafluoroxenates (IV) (Yu. M. Kiselev, N. Ye. Fadeyeva, et al.; DOKLADY AKADEMII NAUK SSSR, No 2, Jul 87)..... | 52 |

LASER MATERIALS

| | |
|---|----|
| Pre-Threshold Destruction of Polymethylmethacrylate Under Action of Laser Irradiation (A. M. Kondyrev, O. F. Pozdnyakov, et al.; KHIMICHESKAYA FIZIKA, No 5, May 87)..... | 53 |
| Thermo-optical Cycles During Resonance Pumping of Carbon Monoxide (V. M. Shmelev, A. D. Margolin, KHIMICHESKAYA FIZIKA, No 5, May 87)..... | 54 |
| Crystallization of Glasses in System ZrF ₄ -BaF ₂ -LaF ₃ -NaF (V. B. Kalinin, Ye. G. Grechko, et al.; FIZIKA I KHIMIYA STEKLA, No 2, Mar-Apr 87)..... | 54 |
| Mathematical Modeling of Formation of Color Centers in Heterogeneous Photochromic Glasses (A. V. Dotsenko, A. V. Morozov, et al.; FIZIKA I KHIMIYA STEKLA, No 2, Mar-Apr 87)..... | 55 |

| | |
|---|----|
| Effects of LiI on Association of Rhodamine 6G Molecules in Isopropanol-CCl ₄ Mixtures (A. M. Saletskiy, V. A. Shekunov, et al.; TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA, No 3, May-Jun 87)..... | 56 |
| ORGANOMETALLIC COMPOUNDS | |
| Synthesis, Structure, and Magnetic Properties of Tri-Nuclear Copper (II) Bis(Hexafluoroacetylacetonate) With Nitroxyl Radical of 4-Phenyl-2,2,5,5-Tetramethyl-3-Imidazoline-1-Oxyl (V. I. Ovcharenko, V. N. Ikorskiy, et al.; ZHURNAL NEORGANICHESKOY KHIMII, No 6, Jun 87)..... | 57 |
| PESTICIDES | |
| Organization of Repair of Chemical Product Storage Areas (M. T. Mironov, M. S. Dylkov, et al.; KHIMIYA V SELSKOM KHOZYAYSTVE, No 6, Jun 87)..... | 58 |
| Alternative to Pesticides (Yevgeniy Gol'tsman; ENERGIYA, No 6, Jun 87)..... | 58 |
| PETROLEUM, COAL PROCESSING | |
| Conversion to Natural Gas Fuel for Motor Vehicles in RSFSR (R. Khadzhiev; SOTSIALISTICHESKAYA INDUSTRIYA, 29 Apr 87)..... | 60 |
| POLYMERS, RUBBER | |
| Acceleration in Polymer Machine Building Industry (V. Dementyev; SOTSIALISTICHESKAYA INDUSTRIYA, 25 Jun 87)..... | 61 |
| Combined Pressure and Shear Strain in Polymer and Rubber Production (N. Yenikolopov, M. Fridman; KRASNAYA ZVEZDA, 28 Mar 87)..... | 64 |
| Journal Issue on Liquid Rubbers (Aleksandr Ivanovich Krashennikov, Vladimir Petrovich Shoboldin; KHIMIYA: ZHIDKIYE KAUCHUKI, No 4, Apr 87).. 68 | 68 |
| Influence of Preliminary Laser Irradiation on Processes of Thermal Oxidative Destruction of Polyacrylonitrile (I. B. Klimenko, N. V. Platonova, et al.; VYSOKOMOLEKULYARNYYE SOYEDINENIYA, No 5, May 87)..... | 69 |

| | |
|--|----|
| Electro-Optical Effects in Comb-Like Liquid Crystalline Polymers | |
| (I. A. Korobeynikova, R. V. Talroze, et al.; VYSOKOMOLEKULYARNYYE SOYEDINENIYA, No 5, May 87)..... | 69 |
| Electro-Optical Effects in Comb-Like Liquid Crystalline Polymers | |
| (I. A. Korobeynikova, R. V. Talroze, et al.; VYSOKOMOLEKULYARNYYE SOYEDINENIYA, No 5, May 87)..... | 69 |
| Pre-Transitional Phenomena and Electrical Birefringence in Isotropic Phase of Liquid Crystalline Polymer With Mesogenic Groups in Side Chain | |
| (Ye. I. Ryumtsev, M. A. Agafonov, et al.; VYSOKOMOLEKULYARNYYE SOYEDINENIYA, No 5, May 87)..... | 70 |
| Anomalous Microscopic Etching of Nitrocellulose Detector Films | |
| (S. V. Stovbun, A. G. Salina, et al.; PLASTICHESKIYE MASSY, No 5, May 87)..... | 71 |
| Radiation-Chemical Oxidation of Polyethylene: Influence of Dose Rate on Mechanical Properties | |
| (A. A. Dalinkevich, S. G. Kiryushkin, et al.; KHIMIYA VYSOKIKH ENERGIY, No 3, May-Jun 87)..... | 71 |
| Mobility of Charge Carriers in Polyolefins | |
| (V. N. Abramov, A. P. Tyutnev, et al.; KHIMIYA VYSOKIKH ENERGIY, No 3, May-Jun 87)..... | 72 |
| Metallization of Polymer Composition Based on Polyphenylene Oxide | |
| (R. E. Ramanauskas, S. A. Barankov, et al.; TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B, No 2, Mar-Apr 87)..... | 72 |
| Paramagnetism of Polymers With System of Conjugated Double Bonds | |
| (M. A. Kozhushner, L. S. Lyubchenko, et al.; DOKLADY AKADEMII NAUK SSSR, No 6, Jun 87)..... | 73 |
| Advances in Polymer Liquid Crystals | |
| (V. P. Shibayev; KHIMICHESKIYE VOLOKNA, No 3, May-Jun 87)..... | 74 |
| Treatment of Cellulose Staple Fibers for Antimicrobial Resistance | |
| (V. I. Shlyakhov, O. I. Pesnya, et al.; KHIMICHESKIYE VOLOKNA, No 3, May-Jun 87)..... | 74 |

| | |
|---|----|
| Synthesis of Polymer Surfactants Based on Derivatives of Naphthalene and Formaldehyde (M. A. Kuchkarova, M. I. Umarova, et al.; UZBEKSKIY KHIMICHESKIY ZHURNAL, No 2, Mar-Apr 87)..... | 75 |
|---|----|

RADIATION CHEMISTRY

| | |
|--|----|
| Laser-Induced Reaction of Yb Atoms With Hydrogen Chloride in Gas Phase (S. K. Borisov, N. A. Karpov, et al.; KHIMIYA VYSOKIKH ENERGIY, No 3, May-Jun 87)..... | 76 |
| Current Developments and Trends in Use of Ionizing Radiation in Biotechnology: Literature Review (A. S. Klimentov; GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST', No 4, May-Jun 87)..... | 77 |
| Non-Equilibrium Ozone Breakdown Under Action of Pulsed IR- Laser Irradiation (N. Yu. Mordkovich, B. S. Lunin, et al.; KHIMICHESKAYA FIZIKA, No 4, Apr 87)..... | 77 |

MISCELLANEOUS

| | |
|--|----|
| Data Base of Biologically Active Compounds (V. Masin; NAUKA I TEKHNIKA, No 2, Feb 87)..... | 78 |
| Computerized Chemical Data Base in Yerevan (N. Ordinyan; SOTSIALISTICHESKAYA INDUSTRIYA, 29 Apr 87)..... | 79 |

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USE OF MICROCOLUMN CHROMATOGRAPHS TO MONITOR CHEMICAL QUALITY

Moscow TEKHNIKA-MOLODEZHI in Russian No 6, Jun 87 pp 27-29

[Article by Vladislav Ksionzhik: "State Examinations for Polymers;" first two paragraphs are TEKHNIKA-MOLODEZHI introduction printed in italics]

[Text] Time has posed the acute problem of the quality of goods produced. Yesterday we hadn't even thought of state acceptance, but today we are already solving the specific social and scientific-technical problems it poses. Comrade M. S. Gorbachev turned young people's attention to them in his speech to the 20th Komsomol Congress.

Achieving new levels of quality is unthinkable without scientifically sound process monitoring methods and an instrument base. Our special correspondent tells of the capabilities of modern analytical instruments.

Even the spoiled princess on the pea seems a lady with no particular complaint compared to Mistress Precision Chemical Technology. The smallest disturbance in process conditions, the slightest change in raw material metering -- and immediately, instead of high-quality products, the plant puts out rejects. What's even more dangerous -- you can't determine the quality of a product, for example, any medicine, by its appearance. White powder. But you wouldn't want to taste test it.

The more complicated the composition of a chemical product, the more difficult it is to learn what's in it and how much. Testing for conformance to GOSTs becomes a complex scientific-technical task.

Of course, spectral analysis makes it possible to quickly and easily determine how much carbon, hydrogen, or oxygen is in a sample. But this method is blind to molecular composition if different polymer substances have been mixed. This is why traditional methods of monitoring quality of petrochemical industry products take many hours (sometimes several days are lost) and are just as complicated as the basic production process.

For example, it takes a long time to dry, mold, and then tear apart samples of rubber hydrocarbon with all available methods.

It's fine if a product's strength characteristics turn out to be within the norm. But if not? How to know in this case what's lacking, what must be added

to the "caldron" to bring it to the condition of a commercial lot?

Meanwhile, the task of analyzing complex substances was theoretically solved long ago. Today chromatographic instruments which make it possible to determine the composition of virtually any mixtures have been firmly substantiated in scientists's laboratories. (About half the working analytical instruments are chromatographs.)

"Hasn't the time come to use them in production to check product quality?"

I asked this question of Vsevolod Viktorovich Shevkunov, assistant head of the Chromatographic Instrument Development Department of the SKB [special design bureau] for Analytical Instrument Building of the USSR Academy of Sciences' Scientific Technical Department in Leningrad.

"Several years ago," he responded, "liquid chromatography, created in the laboratory, was set up at the chemical works in Nizhnekamsk (one of the largest enterprises in the branch). Complex multistage rubber hydrocarbon tests were no longer needed. The molecular composition of samples was determined in a few minutes..."

However, although this was quite a while ago, the instrument has not been widely introduced into production.

The reason for this lack of success, it is believed, is hidden in its design. But to be sure of this, we first have to understand how a liquid chromatograph works.

We Write "Color," But We Mean "Weight"

The basic component of this instrument is the chromatographic column. This is a small tube into which a sorbent -- a very fine powder with special surface properties -- is tightly packed. A special liquid (the so-called eluent) into which the mixture of substances we are interested in is dissolved is pumped through the column.

The dissolved substances are separated in the sorbent. The molecules of some rapidly race through; the others get stuck for a long time.

Why does this happen? Powder particles have a porous, spongy structure. All micropores are about the same size. Let there be two sorts of molecules dissolved in the eluent. The powder (sorbent) is selected so that the smaller molecules occupy the pores, the larger ones don't.

"Curious" small molecules, passing through the column, will enter the pores, remain in them for a certain time, and only thereafter be washed out. The large molecules race over the entire route "on a green light." They are eliminated by the column, as chromatographers say.

To solve the problem of analyzing the mixture, it remains to determine the nature of each of the substances separated by the column. This can be done, for example, by measuring their refraction coefficients.

Why Columns Must "Get Skinnier"

Quite recently a diameter of 4 mm was considered standard for chromatographic columns. It would seem that this is very small. However, a persistent struggle is going on all over the world to reduce their dimensions. And there is nothing surprising about this. The thinner they become, the less scarce and expensive extremely complex-to-manufacture ultra-pure solvents and sorbents will be used during analysis.

Columns with diameters of 2 and 1 mm have already appeared on the world market. But only the Special Design Bureau for Analytical Instrument Building of the USSR Academy of Sciences' Scientific Technical Department has learned to make instruments with a column diameter of 0.5 mm.

On the Way to a 0.5-mm Family

It's not easy to make a good microcolumn. The least roughness on the inner walls of the tube, and its uniformity will be destroyed. The sorbent must be packed with uniform density throughout the entire channel, without empty spaces and clumps.

So far, metal tubing with a very high (to class 12 precision) degree of inner surface treatment has been used to manufacture columns. The required quality was achieved in tubes of 4- and 2-mm diameters...Metal capillaries were a failure.

They decided to reject metal columns and try fluoroplastic tubes also produced in Leningrad as the raw material. The idea worked. The quality of the inner surface of the plastic capillaries left nothing to be desired. Fluoroplastic satisfied chromatographers' highest requirements, even for resistance to aggressive media.

"With fluoroplastic capillaries, today we have the same separation efficiency as with large-diameter metal columns," V. V. Shevkunov told me. But here he warns of hasty conclusions. "Creating capillary columns isn't everything. We have to learn to determine the substances separated in them."

There are many types of optical detectors. (For curious readers I will present their full names: refractometers, fluorimeters, photometers, and spectrophotometers with once-through cuvettes.) However, they all turned out to be unsuitable for working with microcolumns.

The thinner the tube, the less eluent passes through it per unit of time. This means that the volume of the cuvette, the measuring cell where the contents of the liquid are determined, must be decreased. Otherwise the separated substances will mix again.

The size of the cuvette for a 4-millimeter column is tens of microliters. Simple calculation shows that a 0.5 mm-diameter column requires a cuvette of about 100 times less volume.

Since work has to be done with a very small, almost point-sized cell, detector sensitivity must be greatly increased.

But the limit of sensitivity in traditional types of instruments was reached long ago, and no technical tricks have helped measure, let's say, the index of refraction of any substance with an accuracy of more than 7 decimals. Microcolumn chromatography was viewed early on as a declining, low-sensitivity analytical method.

Is this the case? Judge for yourselves. The Leningrad Special Design Bureau has created fundamentally new optical detectors with a cuvette capacity of only...0.07 microliters. However, the sensitivity of the instruments is no worse than that of the old ones, in which the cuvette were hundreds of times larger!

At first the Special Design Bureau developed a laser refractometric detector. (Its design is now protected by patents in many countries.)

It turned out that the laser could theoretically be used to measure the refraction index of a substance with an accuracy to 12 decimals. (One hundred thousand times more accurate than the old detectors.)

Admittedly, the relationship between the parameter to be measured and temperature still prevents achievement of this accuracy. But, nevertheless, the laser refractometer is working successfully. It has been installed in a series KhZh-1309 microcolumn chromatograph.

The next instrument created at the Special Design Bureau was a microcolumn chromatograph with a fluorescent detector (see photo).

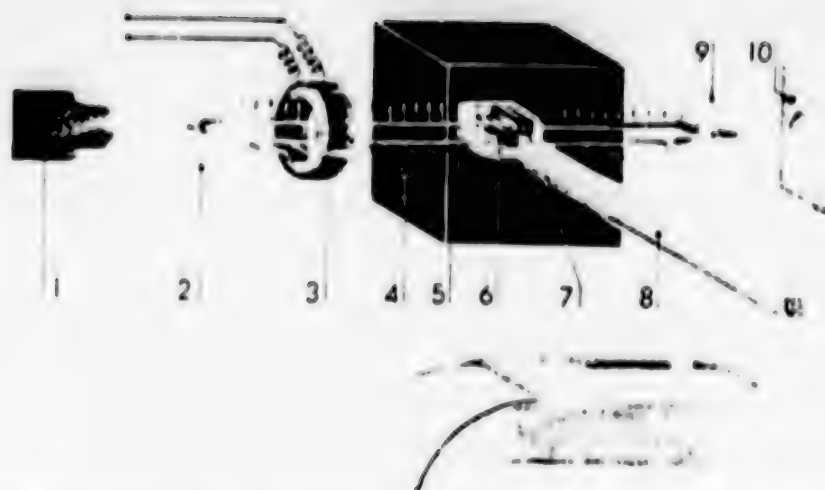
As the name indicates, it is to work with fluorescent, i.e., self-luminous, substances.

It would seem that the instrument's block diagram is simple. It is enough to set the photoelement next to a cuvette with a substance and measure the electrical signal.

But there is so little of the substance in the dish that the light has to be "gathered" literally by quanta. It was in no way possible to permit the possibility of even the least background light in the chamber...

Note that, in addition to unsurpassed sensitivity to fluorescent substances, the instrument possesses one other valuable property. It can perform in gradient chromatography mode.

What is gradient chromatography? Not every mixture can be easily separated in one eluent. It often happens that one solvent is used to separate any two or three ingredients of a multi-ingredient mixture and another to separate the rest. In the new chromatograph this is all combined into one process. The law of continuous change in eluent composition is given. At first, one solvent is supplied, then another is mixed into it, and at the end of the analysis, only the second solvent is active. If the relationship between the concentration gradient and time is properly selected, all components will be successfully separated (even fluorescent substances, well known to chemists for their capricious nature).



In the picture is shown the principal scheme for a laser refractometer mounted on a microcolumn liquid chromatograph (KhZh-1309).

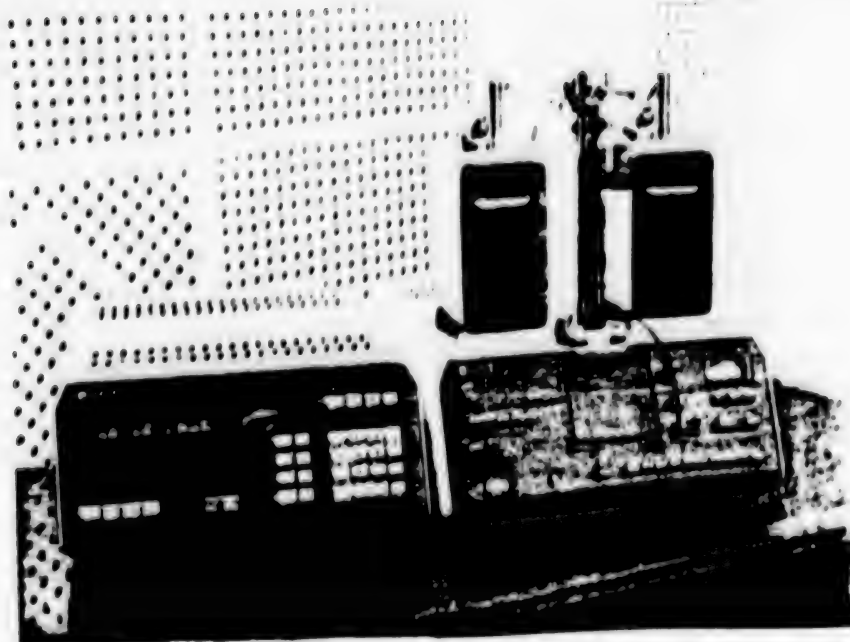
The detector works as follows: The laser beam passes through a polarizer, consisting of a sheet of Iceland spar. In it the beam is separated into two beams of light with mutually perpendicular planes of polarization.

The beams are encoded in an electrooptical modulator. (This helps to eliminate possible interference.) Then one of the beams of light enters the measuring cuvette. The other goes through a cell of similar dimensions which is filled with pure eluent.

The chemical media in microvessels differ. Therefore, the coefficients of refraction for the beams will be different. As a result, a phase difference occurs between the beams, and when they pass through the polarizer, fitted with a mirror-symmetrical input polarizer, the combined beam of light will be elliptically polarized. From the degree of its ellipticity, it is possible to determine the coefficient of refraction for a substance located in the measuring cuvette.

In the diagram, the numbers designate the following:

- 1) Helium-neon laser
- 2) Input polarizing optical block
- 3) Electrooptical modulator
- 4) Thermostatic control block for the refractometer
- 5) Linearly polarized laser beam
- 6) Measuring cuvette with eluent and the sample dissolved in it
- 7) Control cell with pure eluent
- 8) Microcolumn
- 9) Output optical block
- 10) Photodetector



Here the microcolumn liquid chromatograph KhZh-1311 is shown.

One of the most successful examples of the application of the new instrument is separation of a complex mixture of amino acid derivatives. So-called dansyl-derivatives of amino acids (in other words, their debris) float in chemicals, or to be more accurate, in organic broths of complex composition, with which biochemists must often work. The domestic chromatograph's sensitivity to dansyls is an order of magnitude higher than that of the best foreign instruments.

Prediction for Tomorrow: Instruments...

Both Soviet scientists and their colleagues in Bulgaria and the FRG have rated the KhZh-1309 a "10." There are requests for delivery of the instrument to other countries. Series production of the microcolumn chromatograph with a fluorescent detector is being set up...

However, the series of these instruments from plants of the USSR Academy of Sciences' Scientific-Technical Department amounts to no more than 15-20 per year. This is enough only for the largest scientific institutes. At these instrument production rates, it will be a long time until we get to state acceptance of chemical goods.

But is it at all worthwhile using instruments developed for scientific laboratories for production needs? The microcolumn chromatograph costs tens of

thousands of rubles. This is considered intolerably high for a plant instrument.

Remember the Nizhnekamsk Works. A chromatograph from the old series, with a large column, not as advanced and not as expensive as its microcolumn brother, was delivered there.

The instrument performed (and perhaps still does. The Special Design Bureau lost contact with the plant) round the clock. Containers with flammable eluent -- toluene and tetrahydrofurane -- were standing around, recalls V. V. Shevkunov. Per day the chromatograph consumed at least one and a half a liters of scarce ultra-pure solvent, which cost the plant a pretty penny. And if you add the cost of fire protection and other such measures? Wouldn't it ultimately be more advantageous to take a more expensive, but less voracious and simpler instrument?

Even when the work involves toxic substances, the microcolumn chromatograph does not require the traditional attribute of a chemical instrument -- extraction. Counting is done in fractions of a microgram of a sample. The design engineers believe that the instruments are so clean that they can be set up even in a business office.

...And State Acceptance

State acceptance is a state examination which even chemical industry products must take. The evaluation should be fast, objective, and accurate. And microcolumn chromatographs are irreplaceable in cases when we are forced to use scarce eluents and sorbents according to existing procedures, especially if the required grades of chromatographic materials are not produced in this country and must be purchased abroad. And there are almost as many procedures for separating complex mixtures as there are mixtures. Each needs its own eluents, its own sorbents...

We can say in which branches of industry microcolumn chromatographs are required first: at enterprises of the Ministry of the Chemical Industry (to monitor plastics production), the Ministry of the Petroleum Refining and Petrochemical Industry (rubber hydrocarbons), in the food industry, pharmacology, and at enterprises producing biopolymers. The list could go on.

The use of modern analytical methods to monitor products in these areas is already today more an organizational than a scientific-technical problem.

This country is developing scientific instruments which are unique because of the capabilities they possess. Sometimes they remain unique in the sense that only one exists. The label "complicated scientific instrument" frightens away plant laboratories.

Can this be because these instruments require excessively delicately handling? They aren't used to such high precision for instrumentation in the plant... But they must get used to it. Otherwise the problem of raising the quality of goods -- one of the key problems of restructuring -- cannot be solved.

Scientific instrument building, which has for many years absorbed the most advanced of what exists in industry, today must pay back its debt to production.

Last year an inter-branch scientific-technical complex "Scientific Instruments" was formed. The USSR Academy of Sciences' Scientific Technical Department became its head. The opportunity arose to switch many instruments from the category of unique, strictly scientific instruments to series-produced for industry.

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UDC 546.35

X-RAY FLUORESCENT ASSAY OF RUBIDIUM IN SEA WATER

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian
Vol 23, No 2, Mar-Apr 87 (manuscript received 11 Nov 85) pp 174-177

[Article by V. A. Lebedev, U. V. Alvares, A. V. Krasnyanskiy, T. I. Shurupova
and I. V. Golubtsov, Department of Radiochemistry and Chemical Technology]

[Abstract] Rubidium is the second element after potassium which determines the natural radioactivity of sea water. This article suggests an x-ray fluorescent method in combination with preliminary concentration of rubidium by coprecipitation with mixed nickel and potassium hexacyanoferrate to assay the content of rubidium in sea water, with monitoring of the process by the radionuclide ^{86}Rb . The standards used in radiofluorescent assay of rubidium were precipitates of the mixed hexacyanoferrate produced under identical conditions from model solutions with known rubidium content similar to its content in sea water. No systematic deviations were observed. The method is reasonably fast, allowing it to be recommended for use under expeditionary conditions: one analysis requires 1.5-1.6 hrs, and the sediment coagulation time can be significantly reduced by the use of ultrafiltration. References 6: 4 Russian, 2 Western.

6508/9835

CSO: 1841/413

METROLOGICAL ASPECTS OF CHEMICAL ANALYSIS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 42, No 4, Apr 87 pp 581-585

[Article by L. N. Filimonov]

[Abstract] In analyzing the metrological aspects of chemical analysis, three areas of development and application of analytical chemistry must be considered: 1) the development of the theoretical principles and internal capabilities of analytical chemistry itself, 2) the production of sufficiently accurate information on the composition of substances, and 3) the quality

of raw materials and products. There is a clear and urgent need to improve the level of training in the area of analytical metrology for various specialists. Changes in the requirements which must be placed in State standard documents, governing analytical chemistry, are analyzed. Mechanical extension of State standards, developed without the participation of analytical chemists and without considering the specifics of analysis, into the area of quantitative analysis, is senseless. Excessive requirements for accuracy of analytic instruments also make no sense, given that much greater errors are introduced in the selection and preparation of specimens for analysis. Effective approaches are required for metrological certification of analytical instruments, particularly multipurpose devices such as spectrometers. The experience gained in certification of analytical laboratories and recommendation of technical standard documentation, regulating this certification, should be carefully discussed.

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UDC 543.1

SOME FORMALIZED CONCEPTS AND QUANTITATIVE ESTIMATES IN CHEMICAL ANALYSIS BASED ON COMPUTERS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 42, No 4, Apr 87
(manuscript received 10 Nov 85) pp 741-750

[Article by L. A. Gribov, Yu. M. Luzhkov and A. A. Popov, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences; "Khimavtomatika" Scientific-Production Association, Moscow]

[Abstract] Performance of mechanized analytical experiments requires the development of a logically connected and internally noncontradictory system of concepts of analytical chemical principles which are accessible for formalization and subsequent algorithmization. The inherently intuitive and heuristic aspects of such concepts as the analytical task and the domain of its solution, while not preventing the analytical chemist from performing complex analyses using computers, do lack the necessary clarity for computer-based analytical chemistry. It is therefore expedient to begin by formalizing general statements, obvious to the analytical chemist, giving particular attention to their comprehensibility to the computer. Analysis reveals that formalization of the concepts of "selectiveness" and "reliability" of chemical analysis allows development of a strict formulation of criteria for the solution of computerized planning of automatic analytical devices by means of artificial intelligence and permits quantitative evaluation of analytic results by means of a microprocessor without the participation of man. The formalization allows strict formulation of criteria for computerized planning of automatic analytical instruments and the creation of algorithms for the microprocessors to be used in such instruments, which are capable of evaluating the reliability of analytical results independently. Figures 3; references 9 (Russian).

6508/9835

CSO: 1841/417

UDC 541.18

CHARGE OF AEROSOL PARTICLES IN INERT GASES IN PRESENCE OF EXTERNAL ELECTRIC FIELD

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 61, No 5, May 87
(manuscript received 13 Mar 86) pp 1379-1381

[Article by A. V. Zagnitko and A. A. Kirsh]

[Abstract] Experimental data are presented on the unipolar charge of aerosol particles in inert gases with various values of electric field strength E and the product of air conductivity σ and charge time t . The work was performed with particles of dibutyl phthalate with $r = 0.35-1.6 \mu\text{m}$, $E = 40-840 \text{ V/cm}$ in nitrogen containing less than 0.05% O_2 , argon, helium, and in air. In helium and nitrogen the value of γ increases with increasing E , apparently due to the difference in the fluxes of electrons and ions to the surface of the particle as functions of temperature. Similar results were obtained for measurement of the charge of individual particles in nitrogen and air at $E = 83.5, 420$ and 840 V/cm . As the negative potential of the wire corona electrode was varied from 0.7 to 2 kV in helium and 1.8 to 5 kV in argon, the variation of current as a function of σ at $E = 83.5 \text{ V/cm}$ passed through a maximum. In this case the particles were charged differently, resulting in the appearance of positive ions, apparently formed as a result of the interaction of helium and argon atoms with the electrons. Figures 2; references 11: 8 Russian, 3 Western.

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CSO: 1841/416

UDC 547.944/945+547.856.1

SYNTHETIC ANALOGS OF PEGANIN ALKALOIDS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 2, Mar-Apr 87
(manuscript received 14 Nov 86) pp 309-310

[Article by M. V. Telezhenetskaya and A. L. Dyakonov, Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences, Tashkent]

[Abstract] The authors brominated quinazoline alkaloids of peganin (Ia) and deoxypeganin (Ib) with bromosuccinimide in glacial acetic acid. The yield of the products of bromination of both Ia and Ib was 50-70%. Bromination of peganin (Ia) yielded a primary product monobromated at the 6th position of the benzene ring (IIa). Under similar conditions, 6-bromodeoxypeganin (IIb) was obtained from deoxypeganin (Ib). References 3: 2 Russian, 1 Western.

6503/9835

CSO: 1841/439

UDC 541.124/128

23 PHASE PORTRAITS OF SIMPLE CATALYTIC OSCILLATOR

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 61, No 5, May 87
(manuscript received 23 Jun 86) pp 1388-1390

[Article by A. I. Khibnik, V. I. Bykov and G. S. Yablonskiy, Scientific Research Computer Center, USSR Academy of Sciences, Pushchino; Siberian Department Computer Center, Krasnoyarsk; Institute of Catalysis, Novosibirsk]

[Abstract] A detailed parametric analysis is presented of a kinetic model corresponding to an autocatalytic system of reactions:



where Z is an active site on the surface of a catalyst, X and Y are adsorbed substances, and Z' is a secondary form of Z. The system of reactions is assumed to have a high multiplicity of stationary states and auto-oscillations. The model is a system of three nonlinear differential equations based on forward reaction rate constant (K_1) (K_2 , $K=K_{-4}/K_4$ where K_{-1} is the reverse reaction rate constant), bifurcational curves are constructed, and by studying their reconstruction while varying the third parameter (K_4), the remaining parameters (K_1) are determined. In all, 23 phase portraits of the system are found. The parametric analysis shows a great variety of dynamic behavior with respect to the simple kinetic model. Development of the approach for more complex systems will provide a tool for detailed parametric analysis of kinetic models of actual chemical systems. Figures 1; references 14: 13 Russian, 1 Western.

6508/9835

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SPATIAL STRUCTURES IN OSCILLATING REACTIONS OF OXIDIZING TETRAAZAMACROCYCLIC COMPLEXES OF NICKEL AND COPPER AND INFLUENCE OF SURFACE ON REACTIONS

Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 23, No 2, Mar-Apr 87 (manuscript received 19 Mar 86) pp 234-236

[Article by K. B. Yatsimirskiy, L. N. Zakrevskaya, Ya. D. Lampeka, A. G. Kolchinskiy and L. P. Tikhonova, Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] The authors have previously discovered a new type of oscillating chemical reactions--oxidation of tetraazamacrocyclic complexes of nickel and copper with bromate, in which the metal ion periodically changes the degree of oxidation. This article studies the spatial structures arising in the process of such oscillating chemical reactions as well as the influence of properties of the surface in contact with the reaction solution on the oscillating process. The oscillations begin as soon as the substances are mixed, without an induction period. After seven to ten minutes, concentrated nonuniformities appear as dark brown spots on a brownish yellow background. The metal surface was found to influence the process of development of waves. An increase in the oscillating frequency can be caused by catalytic action and by the influence of mechanical surface irregularities. In addition to time-synphased concentrated fluctuations, spatial structures are thus also observed to develop over time. Figures 3; references 5: 2 Russian, 3 Western.

6508/9835

CSO: 1841/416

NONSTATIONARY CATALYTIC PREPARATION OF SULFUR IN KLAUS PROCESS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 6, Jun 87 (manuscript received 18 Aug 86) pp 1424-1428

[Article by Yu. Sh. Matros and A. N. Zagoruyko, Institute of Catalysis, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] A mathematical model was constructed for the recovery of sulfur via the Klaus process, a system involving a series of adiabatic conversions and heat exchangers for cooling gas and condensing sulfur. Nonstationary conditions were created by periodic alterations in the filtration direction of the gas mixture through a stationary catalytic bed. The model was based on the assumption that the formulation $2H_2S + SO_2 \rightleftharpoons \frac{3}{n}S_n + 2H_2O + 100 \text{ kJ per}$

mole of SO_2 describes the overall process, as well as the facts that the partial pressure of sulfur undergoes rapid equilibration, that catalyst

activity is proportional to its surface area, and that inactive grain concentration is directly related to bound sulfur. In the nonstationary mode, the degree of conversion approached 95% with an input of 5% H₂, 2.5% SO₂, and 92.5% N₂ and an inlet temperature of 125°C. In the conventional stationary mode, maximum attainable conversion was on the order of 90.8%, and the requirements were for an inlet temperature of 225°C. Figures 2; references 11: 5 Russian, 6 Western.

12172/9835

CSO: 1841/429

UZSSR CHEMISTS AND CHEMIZATION TASKS

18410477 Tashkent PRAVDA VOSTOKA in Russian 29 May 87

[Article by S. Yunusov, Corresponding Member of the USSR Academy of Sciences and Hero of Socialist Labor, and M. Askarov, Corresponding Member of the UzSSR Academy of Sciences under the "Scientific and Technical Organization, Arsenal of Development" rubric: "Scientists and Chemization"]

[Text] Accelerated development of sectors called upon to assure an output of the national economy at the most advanced industrial boundaries in the world is one of the features of the 12th Five-Year Plan, as noted at the 27th CPSU Congress. The chemical industry, the products of which are used more and more widely in different sectors of industry--in agriculture, construction, and also in homes--is also named among them. Accelerated development of the chemical industry in the Five-Year Plan is specified in conformance with the Integrated Program of Chemization of the USSR National Economy for the Period up to the Year 2000 adopted by the CPSU Central Committee and the USSR Council of Ministers. A radical increase in the quality and reliability of products is planned for the program in practically all sectors of the economy, and this will contribute to an improvement in the living conditions of the Soviet people and a strengthening of the economic and defense strengths of the country.

Chemists of the country have to do substantial work. The collectives of the four chemical institutes of the UzSSR Academy of Sciences understand this. In the first year of the current Five-Year Plan they fulfilled 66 scientific programs and tasks in eight directions. They included 20 tasks of the USSR State committee for Science and Engineering. Our chemists are completing a series of work on the use of natural mineral sorbents for the purification of gases, liquids, and oils and on the synthesis of new water-soluble polymers and surface-active agents.

Scientists of the Chemistry of Plant Substances Institute, researching biostimulants and highly effective chemical substances for plant protection have isolated more than 100 new compounds, a number of which, including allapinene (an antiartemisia preparation patented in France), medamine (for helminthic disease) and tefestrol (for female infertility), in conformance with the recommendation of the USSR Ministry of Health, are undergoing clinical tests at the present time. Butyl captax, a defoliant for fine-fibered cotton, nutritive protein from cotton plant seeds, and lignin preparations are in the stage of adoption.

The Bioorganic Chemistry Institute today is working on serious problems in the field of gene engineering of the cotton plant. Methods of hybrid technology and chromosome analysis have been developed by the collective. Donor material of the DNA of pure genetic lines and wilt-resistant varieties of the cotton plant has been prepared. Scientists have synthesized the pheromone of the cotton cutworm and manufactured 162,000 traps used successfully on the fields of Uzbekistan and Tajikistan. The results of this work offered the possibility for combatting agricultural pests by means of biological methods, at the same time excluding chemical methods. Authorization has been obtained for the sale of licenses for highly purified kikinase and an antiviral preparation of megosin.

However, let us say right out that there are many serious deficiencies in the activity of the chemical institutes which have not been rectified over a period of many years. First of all is the weak link of science with production. As before, coordination is weak between academic, higher institutes of learning, and sector science in the activity of the department and institutes, and there is no integration of the research being conducted, the depth of formulation of basic problems, and the growth of the effectiveness of developments.

The collectives of the institutes work in the old way--passively and inefficiently; they are not able (or do not wish) to use existing resources in their activity. This is the result: if the return from scientific research at the Chemistry of Plant Substances Institute comprised 2 rubles 60 kopecks per ruble of expenditure, at other institutes, such an indicator in all comprised only less than a ruble. And instead of raising the volume of adoption annually, cases exist in which they attempt to include work done long ago which at the same time is added as a progressive effect.

Today the main problem in the program of the activity of scientists is the chemization of all sectors of industry. The Integrated Program of the Chemization of the USSR National Economy for the Period up to the Year 2000 also focuses on this. What does this mean for scientists working in this field of science of our republic? First of all is the provision of cotton growing with new balanced, slowly-dissolving fertilizers with a high coefficient of assimilability of them by plants and growth substances providing healthy development of plants.

In addition, we must give cotton growing nontoxic but effective defoliants, having a systematic action, which during a whole range of annual conditions would cause leaves to fall for a definite period and give a working front for machine harvesting of the crop. Here chemists of the republic have a serious obligation to agricultural workers.

Existing fertilizers, growth substances, and defoliants are justly criticized for low effectiveness and high toxicity. But again, too, existing achievements in this field are reluctantly introduced into production. For example, copper- and zinc-containing fertilizers, preparations of rozalin,

olgin, and the defoliant butyl captax did well in multiyear field tests; however, they are not being produced in the proper amount, and what is being produced is due to the initiative of the authors. And indeed, there are orders for their production on the part of agriculture.

As for substances acknowledged to be toxic, two notions can be used to replace them. The first principal method is to develop new defoliants, which would comply with strict requirements for their use. Under the aegis of scientists at the Chemistry of Plant Substances Institute, a great deal has already been done on this task in this direction. The second method is seen in being able to use correctly, not putting off until tomorrow, the achievements of organic chemists and to expand the possibility of chemical modification.

It is necessary also to acknowledge frankly that in recent times chemists of the republic conspicuously lost those positions which were achieved ten years ago in the field of the development of building materials, even though in this time the number of scientists working in this sector has more than doubled. Let us take the quality of cements and products based on them which are being produced. Today they do not correspond to the growing requirements of hydraulic engineering structures.

Production of ceramics, porcelain, and faience products to be used as structural materials is in a stage of stagnation. Therefore, in the construction of unique buildings, and also in homes, an inclination is observed toward ceramic tiles, sinks, and articles of sanitary subassemblies which are of imported production, while the raw material resources of Angren Basin clay could have provided buildings with high-quality products. There was much more talk about phosphogypsum suitable for the production of building materials, cement additives, the manufacture of grainpipes, and linoleum filler. We think that the transition from words to action should have taken place long ago.

And there is one thing more. The training of science teachers has weakened considerably. There are reasons for this. One of the main ones is the absence of specialized councils for defense of dissertations. It can be observed in the example of defenses at the competition for the academic degrees of the candidate and doctor of sciences on the chemistry of high-molecular compounds. Young people leave with finished dissertations, but they cannot hand them over to the council for the simple reason that we do not have such a thing. Finally, it is possible in principle to defend one's work also in other cities where such councils exist, but indeed, it is not possible for all of them to go away for a long time. Such a situation has also arisen in other divisions of science. And this occurs in our time, in which candidates and doctors of sciences must show practical, specific help on their subject to chemical enterprises. We think that such a situation must not remain, or otherwise we shall lag behind seriously and for a long time.

In the matter of raising the efficiency of scientific developments, the material and technical base in the institutes is of decisive importance. In spite of the enormous efforts of their leaders, up to now this problem has clearly not been resolved, and existing bases do not correspond to present-day

requirements. However, available instruments and equipment have become worn out by 40-50 percent, and there are no spare parts for them.

In January 1987, the Plenum of the CPSU Central Committee required increasing replacement of the arsenal of basic ideas and applied developments. The Plenum considered it necessary to increase the output of the personnel of academic, sector, and VUZ science in carrying out tasks related to comprehensive intensification of production. To pay attention to the work of scientific-production associations and interbranch scientific and technical complexes and to take urgent measures for the improvement of the training of scientific personnel, for the reinforcement of their composition with capable young people, for the creation of conditions for the fruitful work of scientists, for raising technical equipment, and for strengthening its experimental base--such are the most important tasks--of the very near future of the chemists of Uzbekistan. Their solution should not be postponed until tomorrow; it is already necessary to translate them into life today.

12410

CSO: 1841

AIR POLLUTION REDUCTION BY CONVERSION OF PLANT EXHAUST SULFUR DIOXIDE TO
SULFURIC ACID

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 29 Apr 87 p 2

[Article by R. Khadzhiyev under the "Courier of the Scientific and Technical
Organization" rubric: "Acid from Anhydride"]

[Text] Enterprises of the USSR Ministry of Nonferrous Metallurgy emit into
the atmosphere 4.6 million metric tons per year of sulfur dioxide. Units are
now being built for the production of sulfuric acid from sulfur dioxide at
the Ust-Kamenogorsk Lead-Zinc and the Almalyk Mining-Metallurgical Combines.

The Central Board of the Scientific-Technical Association of Nonferrous
Metallurgy has subjected the Orenburg and Murmansk Boards of Scientific-
Technical Associations to serious criticism for intolerable passivity in the
solution of this complex national task. The power engineering and environmental
protection sections of the Central Board have been charged with developing
an integrated program for scientific-technical associations by September 1
for developing and adopting waste-free technology at sector enterprises.

12410/9835
CSO: 1841/361

UDC 532.135:541.182

INFLUENCE OF SURFACE-ACTIVE SUBSTANCES ON RHEOLOGIC PROPERTIES OF DISPERSIONS OF CALCIUM CARBONATE IN ORGANIC FLUORINE MEDIA

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 53, No 6, Jun 87
(manuscript received 20 Nov 85) pp 574-576

[Article by Ye. V. Guseva and F. D. Ovcharenko, Department of Natural Dispersed Systems, Institute of Colloid and Water Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] The purpose of this work was to study the influence of a number of surfactants (perfluoroorganic, fluoroaromatic and fatty monoacids) on the rheological properties of dispersions of calcium carbonate in fluoroorganic media. Rheological studies were performed on a rotating viscosimeter "Reotest-2" at a velocity interval of $1.5-1312\text{s}^{-1}$ at 25°C . It was found that viscosity of the dispersions increased with increasing filler-content. No hysteresis of viscosity was observed. There was practically no change in viscosity in low concentration dispersions; in higher concentration dispersions, viscosity depended on the length of the perfluororadical and quantity of sorbed acid. Introduction of calcium carbonate modified with higher perfluoroorganic acids caused thixotropic structure formation. Viscosity of dispersions increased with storage. The results indicate that the concentration of the dispersed phase and the nature of the modifier have a decisive influence on the rheological properties of calcium carbonate dispersions in fluoroorganic media. Figures 3; references 6 (Russian).

6508/9835
CSO: 1841/431

PMR TESTING OF WATER CONTENT IN HYDRATED INVERTED AEROSOL MICELLE SYSTEMS CONTAINING PROTEIN

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian
Vol 28, No 3, May-Jun 87 (manuscript received 31 Jan 86) pp 287-290

[Article by N. L. Klyachko, A. V. Levashov, K. Martinek, V. A. Polyakov and G. B. Sergeyev, Department of Chemical Enzymology, Department of Chemical Kinetics]

[Abstract] In order to determine the content of water in a protein solution dissolved in octane by means of inverted micelles of a sodium salt of diisooctyl sulfosuccinate, the authors utilized the relationship between chemical shifts of water protons and water content in inverted micelles. Variation in water content in the system was accompanied by significant changes in both water peak width and position in PMR spectra. The introduction of protein into the system was found not to cause redistribution of water. The PMR method is useful for monitoring the degree of hydration of surfactants in the presence of high concentrations of protein and in the production of protein-containing micellar solutions by separation of heterogeneous working systems. Figure 1; references 14: 3 Russian, 6 Western.

6508/9335

CSO: 1841/432

PARAMAGNETIC HYDROPHILIC PROBING OF MULTILAYER LIPOSOMES OF CATIONIC LIPID-LIKE MONOMERS BY PMR METHOD

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian
Vol 28, No 2, Mar-Apr 87 (manuscript received 23 Oct 85) pp 183-186

[Article by V. V. Yegorov, Yu. Ye. Shapiro and V. P. Zubov, Department of High-Molecular Compounds, Yaroslavl Polytechnical Institute]

[Abstract] There has been great interest in the synthesis and study of surfactant monomers with lipid-like structures due to their ability to immobilize biological substances and physiologically active compounds and to model membrane processes. The ^2H PMR spectra of N-dodecyl-N, N-diallylcetylacetoammonium bromides (DAAB) in D_2O were recorded at an operative frequency of 80 MHz. Preliminary experiments revealed that the ^2H NMR spectra of 0.1 mol/l DAAB dispersions in water contained only signals from the $\text{CH}_2 = \text{CH}$, $(\text{CH}_2)_n$, and terminal CH_3 groups. Introduction of Mn^{+2} cations allowed for determination of the ratio of integral intensity of internal and external $\text{CH}_2 = \text{CH}$ signals. The experimentally determined values indicated that the Mn^{+2} cations did not penetrate into the liposomes,

droplets with multilayer shells filled with water. Under nonequilibrium experimental conditions, bilayer vesicular structures of lipid-like monomer derivatives can be produced in water even at high concentrations if the structure of the hydrophobic portion of the lipid-like monomer has sufficient asymmetry. Figures 2; references 9: 5 Russian, 4 Western.

6508/9835
CSO: 1841/413

UDC 536.24:532.135

STRUCTURE OF SHOCK WAVE IN POLYMER LIQUID WITH GAS BUBBLES

Minsk DOKLADY AKADEMII NAUK BSSR in Russian Vol 31, No 4, Apr 87
(manuscript received 29 May 86) pp 324-327

[Article by Z. P. Shulman and S. P. Levitskiy, Institute of Heat and Mass Transfer imeni A. V. Lykov, BSSR Academy of Sciences; Voronezh State University imeni Lenin's Komsomol]

[Abstract] This article presents nonlinear wave-dynamics equations for a gas-saturated polymer fluid by means of a quasi-homogeneous approach and uses the equations to study the structure of a steady shock wave. The carrier phase is considered to be a rheologically complex fluid with relaxation. With certain values of the parameter Λ_1 , $D \neq 0$, even if $\gamma > 1$. This means that in highly viscous polymer solutions with bubbles, an oscillator shock wave structure is possible, even though in a similar viscous newtonian fluid the wave has a monotonic profile. The wave equations produced in this work consider only the rheologic dissipative losses in bubble dynamics and are consequently applicable to finely dispersed or viscous mixtures for which the role of thermal dissipation during pulsations of the entrapped gas is small. References 9 (Russian).

6508/9835
CSO: 1841/413

UDC 541.141.7:541.139:547.567

MAGNETIC EFFECTS IN RECOMBINATION OF RADICAL PAIRS IN REACTIONS OF CARBONYL COMPOUNDS WITH PHENOLS IN MICELLES: INFLUENCE OF RADICAL STRUCTURE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 5, May 87 (manuscript received 13 Nov 85) pp 1003-1008

[Article by P. P. Levin and V. A. Kuzmin, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] A study is made of the influence of a magnetic field and temperature on the kinetics of recombination of radical pairs formed upon quenching of

triplet states in quinones and benzophenone derivatives by ols in sodium dodecylsulfate micelles. The rate constants of geminal recombination of the radical pairs, including phenoxyl and semiquinone or ketyl radicals in the micelles were measured. Recombination was retarded by a factor of up to five in a magnetic field of 3.4 kOe. The introduction of heavy atoms as substituents on the radicals increased the geminal recombination rate constant and decreased the magnetic effect, indicating the importance of spin-orbital interactions in singlet-triplet transitions in the radical pairs. Figures 2; references 17: 5 Russian, 12 Western.

6508/9835
CSO: 1841/421

UDC 543.422

ORDINARY AND RESONANT RAMAN SPECTRA OF METHYL- AND ETHYLSULFOVIOLOGEN IN MICROHETEROGENEOUS SYSTEMS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 61, No 6, Jun 87
(manuscript received 19 Nov 85) pp 1562-1568

[Article by L. M. Kachapina and V. V. Trokhimets, Institute of Chemical Physics, Chernogolovka Branch, USSR Academy of Sciences]

[Abstract] The use of microheterogeneous systems in modeling electron transport chains can increase the effectiveness of a redox system by optimizing contacts between its components. Methylviologen and its derivatives are widely used as electron transport media in modeling electron transport systems. This article studies the influence of a microheterogeneous system (micelles and vesicles) on viologen by raman spectroscopy. Molecules of methylviologen and its derivatives in unreduced and reduced states have intense raman spectra which are easy to interpret. Previous studies have investigated the quenching of luminescence of a sensitizer dissolved in micellar lauryl sulfate by methylviologen, noting significant "bonding" of methylviologen with lauryl sulfate micelles. The authors sought the appearance of the methylviologen di-cation with lauryl sulfate micelles in the spectra. The variation in frequency and half width of the MV^{2+} spectra lines with NaLS concentration indicated that the shifts and expansions of the lines were caused by bonding of MV^{2+} with micelles. The raman spectra of a vesicular system included two depolarization lines coinciding with the frequency of the (ESV⁻) dimer. Raman spectra and electron absorption thus indicate presence of the dimer form of the ESV⁻ radical in the internal volume of the vesicles. Figures 2; references 23: 7 Russian, 16 Western.

6508/9835
CSO: 1841/444

THERMOGRAPHIC STUDY OF ELECTROLYTIC IRON POWDERS OF VARYING CHEMICAL COMPOSITION

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 53, No 6, Jun 87
(manuscript received 18 Oct 85) pp 599-603

[Article by A. G. Zhigotskiy, S. I. Rafoshtinskaya, T. M. Shvets and
I. P. Slutskiy, Institute of Colloid and Water Chemistry, UkSSR Academy of
Sciences, Kiev]

[Abstract] This article presents results of a derivatographic study of highly dispersed iron powders with particles of dendritic shape measuring 0.5-0.3 μm on the long axis, produced by two-layer electrolytic bath precipitation. The thermal properties of the iron powders and kinetic characteristics of the process of their oxidation in air were studied on a derivatograph in the 20-1000°C temperature range. Analysis of the derivatograms showed that as the specimens were heated, they oxidized with most of the oxygen attaching to the metal in the first stage of oxidation at a much higher oxidation rate than in the second stage. The relationship of heat input rate, oxygen access to the surface, and rates of the processes themselves were found to be quite important in studying processes of oxidation of highly dispersed powders. The rates of the processes are governed by the physical-chemical properties of the specimens, including particle dimensions, thickness and density of layers of stabilizers on the surface, content of active metal, and chemical composition of oxide phases. Variation in the conditions of thermogravimetric studies of powders can be used to isolate individual stages of oxidation. The chemical composition of the oxidized metal was close to ferric-ferrous oxide in a 1:1 molar ratio. The nature of the organic substance used to stabilize the surface of the powder significantly influences the structure of the oxide phases formed. Figures 2; references 10: 8 Russian, 2 Western.

6508/9835
CSO: 1841/431

COPRECIPITATION OF CERTAIN MICROSCOPIC POWDERS WITH Ni

Vilnius TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B in Russian No 2,
Mar-Apr 87 (manuscript received 11 Jul 85) pp 3-10

[Article by V. V. Skrobot'skaya-Medyalene and D. K. Ramanauskene, Institute
of Chemistry and Chemical Technology, LiSSR Academy of Sciences]

[Abstract] A study is presented of the variation of coprecipitation of electrically conductive and nonconductive microscopic powders with Ni under various conditions of formation. The behavior of the powders is studied and the inclusion of the powders in composite coatings during electrodeposition is analyzed. Maximum coprecipitation of conductive and hydrophobic powders is obtained at low suspension concentrations, of nonconductive and hydrophilic - at higher concentrations. With increasing acidity of the electrolyte,

coprecipitation of hydrophilic aluminum oxide with Ni decreases strongly, while the opposite is true of hydrophobic powders such as B₄C. As cathode current density increases, coprecipitation of conductive powder increases, while that of nonconductive powder decreases. Coprecipitation of nonconductive powder occurs more easily from sulfate and chloride electrolytes than from pyrophosphate electrolyte. Coprecipitation of powders can be stimulated by modifying the properties of the electric surface layers of the particles and by decreasing their hydrophilicity. Figures 8; references 8: 4 Russian, 4 Western.

6508/9835

CSO: 1841/435

UDC 539.4.19

EXPLOSIVE CHEMICAL REACTIONS OF METALS WITH OXIDES AND SALTS IN SOLIDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 4, Jun 87
(manuscript received 16 Feb 87) pp 912-915

[Article by Academician N. S. Yenikolopyan, A. A. Mkhitarian and
A. S. Karagezyan, Institute of Synthetic Polymer Materials, USSR Academy
of Sciences, Moscow]

[Abstract] Uniaxial compression of solids results in mechanical instability of the system, causing an explosion accompanied by sound, flame, and crushing of the solid particles. Systematic studies of explosive chemical reactions of Al, Mg, and other metals with salts and oxides of various metals have shown that the process is initiated only if the thickness of a tablet of the mixed powder is greater than a certain critical thickness. The explosive phenomenon is usually not observed at stoichiometric metal/salt or metal/oxide ratios. There is also an optimum size of the reacting particles, 0.3-1 mm. Critical explosive pressure decreases with increasing hardness of the materials. The critical explosive pressure is independent of temperature. Metal plus crystal hydrate systems explode at comparatively low pressures (around 5 kbar). Metal plus oxide systems explode with a powerful critical reaction at 10-20 kbar. The experimental data can be interpreted by assuming that the solid in the area of the shock wave is in a special state, differing from the solid, liquid and gaseous states. At the moment of relaxation of elastic stress, the solid becomes highly permeable, and all processes occur with zero activation energy. Figure 1; references 7: 6 Russian, 1 Western.

6508/9835

CSO: 1841/425

KINETICS OF EXPLOSIVE CHEMICAL REACTIONS IN SOLIDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 5, Jun 87
(manuscript received 9 Feb 87) pp 1151-1154

[Article by Academician N. S. Yenikolopyan, A. A. Khzardzhyan, E. E. Gasparyan and V. B. Voleva, Institute of Synthetic Polymer Materials, USSR Academy of Sciences, Moscow]

[Abstract] Explosive chemical reactions occurring in solids during uniaxial compression of tablets pressed from mixtures of powders or extrusion of the powder mixtures through dies occur extremely rapidly, in 10^{-5} - 10^{-7} s. One distinguishing peculiarity of these solid phase reactions is the presence in the system of additional elastic compressive energy, resulting in mechanical instability of the entire system. Experiments were performed to provide direct proof that a shock wave represents the necessary and sufficient condition for excitation of an explosive chemical reaction in a solid. The data obtained indicate that in a mixture of solid powder reagents, the explosive chemical reaction is initiated by the shock wave from mechanical rupture of the tablet and occurs as in a quasi-homogeneous medium. The reaction rate is independent of temperature and pressure, and the reaction rate constant is extremely high. Figures 3; references 4 (Russian).

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CSO: 1841/425

UDC 541.127

PHOTO-HEAT INFLAMMATION OF Cl_2 - F_2 GASEOUS MIXTURES

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 4, Apr 87
(manuscript received 4 Apr 86) pp 514-517

[Article by A. P. Suyetinov and Yu. L. Moskvyn, Institute of Chemical Physics, Chernogolovka Branch, USSR Academy of Sciences]

[Abstract] Irradiation of a Cl_2 - F_2 mixture with a light impulse will lead to inflammation when the degree of chlorine photodissociation exceeds 0.4-0.6%. The only product formed in such inflammation is ClF ; the reactants Cl_2 and F_2 burn out completely. A definite induction period exists in this process: it is an experimentally determined and calculated time interval between the moment of photoinitiation and sharp combustion of the reactants. Photoinitiation of Cl_2 - F_2 combustion with a light impulse is connected with heat self-acceleration of the reaction. Figures 2; references 5: 3 Russian, 2 Western (1 by Russian authors).

7813/9835
CSO: 1841/414

PARAMETERS OF FOCAL-PULSATING COMBUSTION OF NITROGLYCERIN POWDER

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 4, Apr 87
(manuscript received 18 Mar 86) pp 530-537

[Article by V. N. Marshakov, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] The theory of focal-pulsating combustion was proposed some twenty years ago, but up to now it has not received adequate experimental or theoretical treatment. An analysis of literature data on nitroglycerin powder N is reported. According to this theory, powders burn by individual foci appearing and disappearing with certain regularity. A focus, although being an inseparable whole, is a condensed phase with a heated and a reactive layer and the flame focus itself, which is located directly above the combustion surface. Depending on experimental conditions, they may be a few microns in size to several millimeters; the combustion rate oscillates between minima and maxima. Nitroglycerin powder burns, forming colorless fibers. The size, strength, and number of these fibers depends on powder composition and pressure. The combustion front has a cellular structure of varying shape. The combustion rate of the powder in each focus cannot be determined directly, and several methods of estimating it were reviewed. The temperature of focal surface combustion was determined with thermocouples and gave a wide range of values, the average of which was $340 \pm 35^\circ\text{C}$. Frequency of pulsation is also difficult to establish, but at least two groups were identified, based on a correlation between pulsation frequency and pressure. Depending on the method used, one can observe pulsations with significantly different frequencies at different pressures. Figures 5; references 19: 18 Russian, 1 Western (by Russian authors).

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UDC 532.529.516

INFLAMMATION OF FUEL FILMS BEHIND SHOCK WAVES

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 5, May 87
(manuscript received 9 Jun 86) pp 702-706

[Article by B. Ye. Gelfand, S. M. Frolov, A. N. Polenov and S. A. Tsyganov, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] The conditions for the appearance of intensifying pressures and for the realization of stationary detonation have not previously been determined in the system liquid film-oxidation gas. The effect of physical-chemical factors on film inflammation in shock waves has not been evaluated nor the

effect of admixtures and impurities. It was of interest to compare the characteristics of auto-inflammation of droplets and films. Various liquid fuels were used in the study in an air and oxygen atmosphere. The experiments have shown that all conditions being kept equal, the films inflamed faster than the droplets. Based on analysis of the characteristic rates of physical-chemical processes occurring during film inflammation, conclusions were reached which were supported by experimental data: the length of the reaction zone for a detonation wave in a system with a thin film or a thick one should be similar; the detonation rate is only weakly related to initial pressure in the system. Figures 3; references 15: 11 Russian, 4 Western (1 by Russian authors).

7813/9835

CSO: 1841/414

UDC 536.46

ASYMPTOTIC THEORY OF STATIONARY COMBUSTION WAVE

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 5, May 87
(manuscript received 28 Jul 86) pp 681-691

[Article by S. I. Khudyayev, Institute of Chemical Physics, Chernogolovka Branch, USSR Academy of Sciences]

[Abstract] The terms combustion wave, flame front, or, even simply, flame are used interchangeably in literature as synonyms describing the zone of chemical conversion. This definition points out the asymptotic character of the science of flame spread in which chemical reactions, occurring close to the frontal zone are studied. In the present paper, construction and validation of the asymptotics of a stationary combustion wave were reported for a single stage exothermal reaction of the n -th order in gas ($Le > 0$, Le = Lewis number) and a condensed medium ($Le = 0$). It was shown that simple construction by the method of joint asymptotic expansions leads to correct asymptotics only for $n \leq 1$. For $Le = 1$ and $Le = 0$, when only one equation has to be solved, the estimate of error for the principal term at $n \leq 1$ was given. It was noted that for $n > 1$, simple construction does not lead to asymptotics for both $Le > 0$ and $Le = 0$. References 31: 26 Russian, 5 Western (2 by Russian authors).

7813/9835

CSO: 1841/414

METHYLDINITRAMINE THERMOCHEMISTRY AND ENTHALPY OF FORMATION OF METHYLNITRAMINE RADICAL

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 295, No 2, Jul 87
(manuscript received 29 Oct 86) pp 419-423

[Article by Ye. A. Miroshnichenko, L. I. Korchatova, E. L. Korsunskiy, B. S. Fedorov, Yu. D. Orlov, L. T. Yeremenko, Yu. A. Lebedev, and Corresponding Member of the USSR Academy of Sciences F. I. Dubovitskiy, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] Studies were conducted on the standard enthalpies of methyldinitramine combustion and evaporation and the enthalpy of formation of the methylnitramine radical. The enthalpy of combustion of methyldinitramine was determined at -823.8 ± 0.7 kJ/mole, and the standard enthalpy of formation at 1.5 ± 0.7 kJ/mole. The enthalpy of evaporation was ascertained to be 52.0 ± 0.4 kJ/mole, and the enthalpy of sublimation of 67.4 ± 0.4 kJ/mole. The energy of activation for the dissociation of the N-NO₂ bond was assessed at 118.4 ± 4.2 kJ/mole. Finally, the enthalpy of formation of the methylnitramine radical was determined at 137.7 ± 5 kJ/mole. Tables 3; references 15: 11 Russian, 4 Western.

12172/9835
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UDC 621.3.032.37

THERMALLY STIMULATED CURRENTS IN METAL 1-GLASS CERAMIC METAL 2 SYSTEMS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 4, Jun 87
(manuscript received 3 Jul 86) pp 898-901

[Article by Academician of the BSSR Academy of Sciences V. A. Belyy,
Yu. I. Voronezhnev, V. A. Goldade, L. S. Pinchuk and V. V. Shardina,
Inst'tute of Metal Polymer System Mechanics, BSSR Academy of Sciences, Gomel]

[Abstract] A study is made of thermally-stimulated current (TST) which arises when glass ceramics are in contact between two dissimilar metals and of variation in TST with glass ceramic structure. Glass ceramics used in the study were based on the oxides $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. Thermally-stimulated currents were measured with the glass ceramics in contact with electrodes made of metals differing in standard electrochemical potentials. Structural heterogeneity was recorded along lines perpendicular to the plane of the electrodes. Heterogeneity results from the appearance of electrical non-equilibrium states in the glass ceramics, detected upon thermal depolarization of specimens and evoked by the varying dissociation energy of the different crystalline and vitreous phases. Restoration of equilibrium occurs by an ion relaxation mechanism, accompanied by movement of charge carriers within the specimen, causing the appearance of thermally-stimulated current. Modification of glass ceramics by electrical polarization while they are in contact with dissimilar metals can be used as one method of local regulation of the phase composition of the glass ceramics. Figures 2; references 7 (Russian).

6508/9835

CSO: 1841/425

INFLUENCE OF NATURE OF LIPID AND VIOLOGEN ON TRANSMEMBRANE ELECTRON TRANSFER
IN VESICULAR PHOTOSYSTEM: ELECTRON DONOR - $\text{Ru}(\text{bipy})_3^{2+}$ - VIOLOGEN -
OXIDIZER

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 5, May 87 (manuscript received 16 Oct 85) pp 1011-1014

[Article by Ye. Ye. Yablonskaya and V. Ya. Shafirovich, Institute of
Chemical Physics, Chernogolovka Branch, USSR Academy of Sciences]

[Abstract] An attempt was made to influence the rate of transmembrane electron transfer by changing the structure of the lipid and viologen and the solution temperature. When a sufficient quantity of oxidizer was added to vesicles containing $\text{Ru}(\text{bipy})_3^{2+}$, EDTA and viologen, the effective rate constant for viologen radical disappearance reached a limiting value independent of quantity and type of oxidizer present. Oxidation of the viologen radical with an oxidizer thus occurs in a nonlimiting stage, and the rate constant can be interpreted as the effective rate constant of transmembrane electron transfer. The break on the curve showing variation in the transmembrane electron transfer rate constant as a function of temperature coincides with the phase transition of the lipid from the gel state to the liquid crystal state. The rate constant is independent of the structure of the viologen electron transfer agent. Figures 2; references 13: 2 Russian, 11 Western.

6508/9835

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NUCLEAR MAGNETIC RESONANCE OF ^7Li AND ^{119}Sn IN DOUBLE OXIDES Li_2TiO_3 and
 Li_2SnO_3

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 32, No 6, Jun 87
(manuscript received 30 May 86) pp 1315-1320

[Article by A. A. Vashman, I. S. Pronin, L. V. Golubeva, N. V. Porotnikov,
and K. I. Petrov]

[Abstract] The double oxides Li_2TiO_3 and Li_2SnO_3 are compounds with significant conductivity, particularly at elevated temperatures, and have the properties of solid electrolytes, in which electrical charge transfer occurs by means of the lithium ions. A study is reported of the variation of spin-lattice relaxation time with temperature and of ^7Li and ^{119}Sn NMR spectra for Li_2TiO_3 and Li_2SnO_3 in the 300-520 K temperature range to determine the parameters of ion movement in the crystalline lattice. Analysis of the experimental data and theoretical models for spin-lattice relaxation rate and the second moment are used to establish the characteristic parameters of the

structure and dynamics of the lithium and tin ions. Li^+ is found to interact upon collision over the distance of the radius, indicating that the concept of an "ion fluid" created by the conductivity ions can be extended to Li_2TiO_3 and Li_2SnO_3 . Figures 2; references 6: 4 Russian, 2 Western.

6508/9835
CSO: 1841/419

UDC 541.136.3

SEALED LEAD-HYDROGEN BATTERY

Moscow ELEKTROKHIMIYA in Russian Vol 23, No 5, May 87
(manuscript received 20 Dec 85) pp 682-685

[Article by B. I. Tsenter and N. Yu. Lyzlov, Leningrad]

[Abstract] A detailed study was made of the behavior of a sealed battery, containing a lead dioxide electrode in a sulfuric acid solution in a hydrogen atmosphere. Studies were performed by the rotating disk electrode method, semisubmerged electrode method, and porous electrode volt-ampere method using high hydrogen pressure chambers. A lead dioxide electrode in contact with molecular hydrogen was found to have certain behavioral peculiarities in comparison to its behavior in aerated electrolytes. A lead-hydrogen battery is suggested which has certain advantages over other known metal-hydrogen batteries. The hydrogen electrode is more active than in previous designs, and the battery charge is better preserved over time. The better charge preservation and lower cost indicate that the lead-hydrogen battery is quite promising as an electric power source for independent power supplies. Figures 3; references 12: 5 Russian, 7 Western.

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CSO: 1841/417

NONADAPTIVE NATURE OF INFLUENCE OF NONAQUEOUS ELECTROLYTE COMPONENTS ON
ELECTROCHEMICAL BEHAVIOR OF LITHIUM

Moscow ELEKTROKIMIYA in Russian Vol 23, No 5, May 87
(manuscript received 10 Apr 86) pp 701-705

[Article by Ye. M. Shembel, I. M. Maksyuta, and O. S. Ksenzhek,
Dnepropetrovsk Institute of Chemical Engineering imeni F. E. Dzerzhinskiy]

[Abstract] A study is reported of the influence of the composition of a non-aqueous electrolyte containing sulfur dioxide on the resistance of the passivating film on the surface of a lithium electrode as measured with alternating current. All measurements were performed in an atmosphere of dry argon. The influence of DMSO was also studied, indicating that the addition of DMSO caused significant depassivation of the lithium surface. A table compares the resistance of the passivating film as determined by impedance measurements in various electrolytes, indicating that the influence of the solvent on the resistance of the passivating film depends on the presence in the solution of sulfur dioxide and the nature of the solvent. For example, acetonitrile in solutions not containing SO₂ decreases the resistance of the passivating film, while in solutions with SO₂, the introduction of acetonitrile causes additional passivation of the surface. Figures 4; references 6: 4 Russian, 2 Western.

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REARRANGEMENTS OF COMPLEX COMPOUNDS AND QUINONE ON SURFACE OF MODIFIED ELECTRODES

Vilnius TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B in Russian No 1, Jan-Feb 87 pp 141-142

[Synopsis of deposited paper by A. S. Gudovichyus, V. I. Razumas, and Yu. Yu. Kulis, Biochemistry Institute of the LaSSR Academy of Sciences, Vilnius, 1986, 26 pages (Manuscript deposited at the All-Union Institute of Scientific and Technical Information 25 Feb 86, No 1278-86)]

[Text] Polymer layers formed during the modification of a gold surface by polyethylenimine, methylviologen, or benzylviologen have been studied by the methods of cyclic voltamperometry and rotating disc electrode.

It was established that as a result of modification, positively-charged polymer membranes are formed on the metal surface. The electrochemical reversibility of the oxidation-reduction system is enhanced considerably in the case of the electrostatic reaction of the membranes with a negatively-reacting substance, and the electrode process is limited by transport of the substance through the diffusion layer. If the electrostatic reaction is absent or weakly manifested, the electrode process is limited by the transport of the substance through the polymer membrane. The permeability of the membrane to different modifiers varies from 6.99×10^{-2} to $1.32 \times 10^{-3} \text{ cm}^{-1}$ and depends on the dimensions of the reacting molecules.

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12410/9835

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ESTONIAN SUPERPHOSPHATE FERTILIZER PRODUCTION PROBLEMS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 12 Jun 87 p 2

[Article by V. Tsion, TASS correspondent, Maardu, Estonian SSR, under the title "As Many Problems as There Are Granules"]

[Text] Clad in our heavy boots, wide pants made of a dense fabric, thick jackets with double clasps, respirators, and helmets, we approach a massive metal door. I hear the whisper of an elderly woman who is looking at us: "This is the first time in my 10 years here that I see someone coming here of his own free will..."

"Well, let's go," commands Mikhail Seyfetdinov, an expert in power engineering, and forward we go through the half-open doors of the granulated superphosphate shop at the Maardu Chemical Plant of the "Estonfosforit" Association.

Excerpts from a conversation with P. Nikopenzius, chief engineer of the association:

- Our enterprise supplies the nation's entire Northwest with mineral fertilizers. In the first quarter, we churned out five thousand tons of tricalcium phosphate and simple superphosphate in excess of the planned quota. True, production of granulated superphosphate fell short by 17 thousand tons. But the high labor turnover in the shop combined with inexpert use and frequent breakdowns of the equipment are putting us in a spot.

It takes a long time for the eyes to get used to the darkness. We see the hazy outline of Seyfetdinov's back about three meters ahead. The soles of our shoes leave deep footprints in the thick layer of dust. The dust is not just under our feet, but all around us, getting into the respirator, under our tightly closed jacket collars, and into our eyes.

There are huge bunkers, rotating granulator drums, narrow, twisting staircases, hanging conveyer belts, and a chaotic web of pipes. Where are the workers? More than one hundred people work in the shop, 20 employees per shift.

"All of the servicing personnel are at the main control console," explains M. Seyfedinov, having literally read my mind. "The air is cleaner there. And if anything happens, they come down to the shop."

A group of boys and girls wearing the same type of protective uniform as I, sat in a circle in the spacious operator room, trying not to disturb those on duty. You can get by without a respirator here. A red light flashes from one of the circuits on the panel: the mixture is not going from the granulator to the dryer. Equipping themselves with long metal rods, repair workers head for the shop. They will try to punch through the clog in the pipe manually...

Excerpt from the conversation with Nikopenzius:

We use schistous ash instead of lime as an additive during the process of producing granulated phosphate: Estonia has it in abundance. There is a shortcoming to it, however--a deviation from the set parameters of the process is all it takes to clog the pipes with the capricious mixture, which in turn disrupts the production process.

Excerpt from a conversation with workers in the shop:

"All of us are recent graduates of chemical tekhnikums and occupational technical institutions. We were ordered to come to 'Estonfosforit' and forced to work here. Meaning--in the 'granulated superphosphate' shop, where the danger level is highest. Of course there are benefits to go along with this: retirement comes 10 years earlier, and you get bonuses and special food. Pay is excellent when the plan is fulfilled. But fulfilling the plan is no easy proposition given our lack of work experience.

"The shop has been operating since 1970, and most of the mechanisms have 'come of age'. Will we remain in the shop upon expiration of the allocated deadlines? The answer is no, barring any radical change, of course..."

Excerpts from a conversation with V. Nekrasov, head of the shop:

"A sensible project for reconstructing our ventilation system was drawn up but ended up being shelved for four years by the Association management. They forgot all about it. Getting caught up in the daily grind, in the never-ending race to keep up with the plan, they also forgot about the people who make sure the plan is fulfilled. I want and--most importantly--know that I will be able to improve the situation in the shop. The plan is as follows. We will create standard labor conditions for the existing equipment. This will give us the right to require higher-quality work from the Association, especially with respect to repairs. Heightened supervision and additional incentives offered under the new wage system, which went into effect at the Association on April 1, will also help.

"And at the end of the current Five-Year Plan, we will start building a new shop, using what is known as continuous-flow fertilizer production, a

progressive process not requiring warehouse storage. By that time, I hope a top-notch, expert labor team will have been assembled here. And we think that we will be able to make up for the 17 thousand ton shortfall in artificial manure, incurred in the first quarter, by the end of the year."

Commentary of M. Ollino, chairman of the rayon people's control committee:

"The new shop supervisor was right on target: the important thing to do now is to create acceptable labor conditions first and then address production-related problems and the capital repair of equipment. People come first. My only advice would be for him to rely with confidence on assistance from social organizations and on members of the people's control shop group. Nekrasov is right when he states in his assessment of the Association management's position that of late it has paid too little attention to production conditions and did not take measures in response to signals sent out by the people's controllers. And, hence, we have what is the logical consequence of such an approach: the Association ended up owing a lot of granulated superphosphate to the State. This is yet another reminder to all managers who forget about people in their quest to fulfill the plan."

13126/9835

CSO: 1841/399

UDC 661.525.324-403.099.2, 661.5-403.099.2

PRODUCTION OF GRANULES SUITABLE FOR ENCAPSULATION BY THIN POLYMER FILMS FROM
MELTS OF NITROGEN-CONTAINING FERTILIZERS WITH MAGNESIUM-IRON ADDITIVE

Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 6, Jun 87

[Article by A. L. Taran, A. V. Taran and Yu. M. Kabanov]

[Abstract] Slow-acting granulated nitrogen-containing fertilizers encapsulated in thin films of insoluble polymers are manufactured using large (3-4 mm) strong (1000-3000 g/granule) fertilizer granules with smooth spherical surfaces. Introduction of modifiers to increase the rate of seed formation and decrease the rate of crystal growth can increase the yield of such crystals without the characteristic channel which connects the shrinkage cavity in the center of the crystal to the surrounding atmosphere and prevents proper coating of the capsules. A test of numerous potential additives indicates that best results are achieved by the use of a magnesium-iron additive, introduced into the melt as a mixture of finely dispersed particles, measuring 20-40 μm , of magnesite and iron (III) oxide. The presence of even small quantities of Mg^{2+} and particularly Fe^{3+} in an ammonium nitrate melt decreases the rate of crystal growth and increases melt viscosity by more than 20%. Similar results were achieved with a carbamide melt. The granules, without shrinkage cracks, dissolve more slowly, yielding longer-acting fertilizers. The Belorussian "Azot" Production Association is currently preparing to test the magnesium-iron additive process for introduction into production. Figures 4; references 12 (Russian).

6508/9835

CSO: 1841/441

PROSPECTS FOR USE OF LIME-AMMONIUM NITRATE AND SELENIUM

Moscow KHIMIYA V SELSKOM KHOZYAYSTVE in Russian No 6, Jun 87

[Article by E. Ye. Khavkin, doctor of biological sciences]

[Abstract] A Soviet-Finnish symposium on the title subject was held on 26 Jan 87 at the All-Union Scientific Research, Design, and Technological Institute of Chemistry, involving personnel from Soviet research institutes and the "Kemira" Company of Finland. Great attention was given to lime-ammonium nitrate, a commonly used fertilizer. The fertilizer is less explosive than ammonium nitrate, contains two forms of nitrogen, and is more effective than potassium nitrate, urea, or anhydrous ammonia. Lively discussions were held concerning the practicality of using lime-ammonium nitrate in the USSR. Its lower nitrogen content than other fertilizers increases transportation costs, and some persons present thought it would acidify the soil. Only large-scale studies can answer the question of desirability of producing and using the substance in the USSR. The Kemira Company has begun to add selenium to fertilizer to food crops because of a selenium deficiency in the Finnish diet, which can lead to cardiovascular disease and increase the risk of cancer.

6508/9835

CSO: 1341/438

UDC 543.422

AUGER ELECTRON SPECTROSCOPY OF TITANIUM FILMS ON DIAMOND SURFACE

Moscow POVERKHNOST: FIZIKA, KHIMIYA, MEKHANIKA in Russian No 6, Jun 87
(manuscript received 25 Sep 86) pp 146-148

[Article by V. G. Aleshin, A. G. Gontar, A. A. Smekhnov, and D. V. Sokolyuk,
Institute of Superhard Materials, UkSSR Academy of Sciences, Kiev]

[Abstract] Methods of auger electron spectroscopy and secondary ion mass spectroscopy are used to study titanium films 50-80 nm thick on the face (111) of synthetic diamond in an unheated vacuum system. Films were applied at $1 \cdot 10^{-2}$ Pa with a planar magnetron system at 2 nm/s at 300, 500, and 700 K diamond surface temperatures. Layers of titanium oxides of variable composition, depending on diamond surface temperature, were formed. The zone of formation of titanium carbides increases with increasing substrate temperature due to diffusion processes and activation of the carbide-formation reaction. Figures 3; references 5: 3 Russian, 2 Western.

6503/9835

CSO: 1841/419

UDC 539.143, 144'539.193

QUADRUPOLE INTERACTIONS IN NMR RELAXATION OF KSbF_6

Novosibirsk ZHURNAL STRUKTURNY KHIMII in Russian Vol 28, No 2, Mar-Apr 87
(manuscript received 6 Feb 86; with revisions 15 Apr 86) pp 180-182

[Article by S. G. Kozlova, Yu. G. Kriger, and V. K. Goncharuk, Institute of Inorganic Chemistry, Siberian Department, USSR Academy of Sciences]

[Abstract] Primary attention is given in this work to the physical properties of the low-temperature cubic KSbF_6 phase. Measurements of the temperature dependence of quadrupole bond constants on ^{121}Sb nuclei, spin-lattice relaxation T_1 of ^{19}F nuclei, and dielectric permittivity $\epsilon(T)$ were performed in polycrystalline KSbF_6 specimens synthesized by the reaction of $\text{KSb}(\text{OH})_6$ with

liquid KF and by reaction of KF with SbF_5 in a solution of BrF_3 . The strong anisotropy of reorientation of the almost regular SbF_6^- octahedron observed can be interpreted by means of a model in which the Sb ions are displaced from the center of symmetry of the SbF_6^- anions, while the anisotropy of reorientation results from the existence of electric dipole moments in the SbF_6^- anions. This assumption agrees with measurements of dielectric permittivity $\epsilon(T)$ for KSbF_6 . The behavior of $\epsilon(T)$ in the area of the phase transition indicates that the phase transition in KSbF_6 is a ferroelectric transition as described by Casabella [J. Chem. Phys., 1964, 40, 149]. The conclusions of this article agree with the suggestion of Heyns and Reynhardt [J. Phys. Chem. Solids, 1981, 42, 461], in which the low temperature phase is classified as piezoelectric and optically active. Figures 2; references 13: 3 Russian, 10 Western.

6508/9835

CSO: 1841/419

UDC 66.049

MECHANOCHEMICAL ACTIVATION AND DIMENSIONAL EFFECT IN DISSOCIATED SUBLIMATION OF SOLIDS

Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 60, No 5, May 87
(manuscript received 12 Sep 85) pp 1205-1208

[Article by V. A. Ilyin, V. I. Kolynina, Yu. M. Tairov and V. F. Tsvetkov,
Leningrad Institute of Electrical Engineering imeni V. I. Ulyanov (Lenin)]

[Abstract] Mechanical activation, leading not only to acceleration of sublimation, but also to changes in the chemical composition of the vapor phase, has never been studied theoretically or experimentally. The effect was first observed by the authors in studies of dissociative sublimation of silicon carbide grains and should occur for a number of other materials. The phenomenon is related to the defect content of grains, resulting from crushing of the material. It is shown for the first time that mechanochemical activation significantly changes the composition of the vapor phase. This strongly influences mass transfer processes related to the growth of silicon carbide single crystals, sintering of polycrystalline products based on the crystals, and the thermodynamic functions of the substance. The effect should also be observed for other solids with molecular vapors. Figures 3; references 7: 5 Russian, 2 Western.

6508/9835

CSO: 1841/421

MAGNETISM OF MIXED RARE EARTH AND URANIUM SELENIDES OF COMPOSITION
 $\text{Ln}_2\text{U}_2\text{Se}_7$ (Ln = Tb, Dy, Ho, Er)

Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 26, No 2
 May 87 (manuscript received 28 Nov 85) pp 329-332

[Article by D. G. Barakadze, V. I. Chechernikov, Z. E. Chachkhiani,
 P. V. Nutsubidze and V. K. Slovyanskikh, Georgian Polytechnical Institute
 imeni V. I. Lenin]

[Abstract] Results are presented from a study of the magnetic properties of new mixed uranium and rare earth selenides of the composition $\text{Ln}_2\text{U}_2\text{Se}_7$, where Ln = Tb, Dy, Ho, Er. The compounds were produced by the gas transport method in quartz ampoules from mixtures of $\text{LnSe}_{1.4}$ and $\text{USe}_{1.9}$ with iodine as the transporting reagent. Magnetic properties were studied at up to 10 kOe at 4.2-300 K on a vibration magnetometer and in magnetic fields of up to 100 kOe at 4.2 K on a "Solenoid" apparatus. In compounds with heavy rare earth elements, magnetic ordering is absent down to 4.2 K with specific magnetic susceptibility following the Curie-Weiss law from 60-300 K. The paramagnetic Curie point Θ_p of all compounds was positive, increasing from Er to Tb. Effective magnetic moments for molecules of the compounds were determined. The magnetization curves indicate that in strong magnetic fields, magnetization approaches saturation, which agrees with the theoretical and experimental data for paramagnetic substances. Figures 3; references 6: 5 Russian, 1 Western.

6503/9835
 CSO: 1841/421

UDC 549.211

STRUCTURAL IMPURITIES AS INDICATORS OF GROWTH MECHANISM OF NATURAL DIAMOND CRYSTALS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 4, Jun 87
 (manuscript received 1 Apr 86) pp 868-871

[Article by G. K. Blinova, Central Scientific Research and Geological
 Prospecting Institute of Nonferrous and Noble Metals, Moscow]

[Abstract] Structural impurities can be considered as indicators of the formation conditions of diamonds. The major purpose of this work was to study hydrogen centers and their role in the process of diamond crystallization. These centers appear in the IR spectra of diamonds as narrow absorption bands around 3107 and 1405 cm^{-2} . The data indicate that hydrogen, chemically adsorbed by a growing face, blocks the layer development of diamond. Structural hydrogen impurities are regularly distributed in natural diamonds and are a more sensitive indicator of the conditions and mechanism of crystal growth than are nitrogen centers, which apparently can

be transformed in the post-crystallization period. The diffusion and transformation of structurally bonded hydrogen is less probable than that of nitrogen [C-N] due to the greater C-H bond strength. Figures 2; references 11: 7 Russian, 4 Western.

6508/9835
CSO: 1841/425

UDC 548.9:537+537.533

DISLOCATION-FIELD MECHANISM OF POST-EMISSION OF ELECTRONS AND POSITIVE IONS
FROM THE FRACTURED SURFACE OF AN LiF SINGLE CRYSTAL

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 5, Jun 87
(manuscript received 14 Jul 86) pp 1161-1164

[Article by A. G. Lipson, V. A. Kuznetsov, D. M. Sakov, V. A. Klyuyev, Yu. P. Toporov and corresponding member of the USSR Academy of Sciences B. V. Deryagin, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] An attempt is made to establish the mechanism of simultaneous post-emission of electrons and positive ions from the fractured surface of an LiF single crystal and its relationship with the electrification of the freshly formed surface. The electrophysical processes occurring on an LiF fractured surface were studied in sequence, beginning with the moment of fracture. Post-emission drops to the background level in five to ten minutes after fracture of the crystal. An electrical charge continues to be recorded with little change for at least one hour after fracture. A mechanism is suggested for simultaneous emission of an electron and positive lithium ion into a vacuum: edge dislocations moving in the force field separate electrons from F centers, which form upon fracture in the surface layer of the crystal. As a dislocation reaches the surface, the electrons it transports may be emitted into the vacuum, due to the Auger energy redistribution process between dislocation electrons, as one of them enters a deep trap (σ center) and the energy liberated is transmitted to another electron. Departure of an electron from the dislocation trap results in the appearance of an excess positive charge at that point on the surface, causing expulsion of one of the lithium ions from the σ center by electrostatic forces. Figures 3; references 12: 10 Russian, 2 Western.

6508/9835
CSO: 1841/425

INFORMATION CONTENT OF SPEEDS OF SOUND IN SINGLE CRYSTALS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 61, No 5, May 87
(manuscript received 29 Nov 85) pp 1344-1348

[Article by Yu. M. Sokolskiy, Leningrad State Scientific Research and Design Institute of the Basic Chemical Industry]

[Abstract] A study is reported of the influence of forces of chemical reaction on the speed of sound in a single crystal. The presence of such a connection allows the value of the speed of sound to be used for quantitative estimation of structural features of chemical compounds. The speed of sound is inversely proportional to density with a constant elastic modulus. Since the modulus of elasticity is determined primarily by reactions between particles, i.e., chemical bond forces, the variation of velocity as a function of density is the same only in groups of substances of similar chemical composition with approximately identical chemical bond forces. Even within such groups, the ionic nature of the bonds changes, indicating an anibatic nature of changes in velocity and density. For substances with different chemical bond forces, even with identical chemical compositions, changes in velocity and density are symbatic. When crystals are dissolved in water, the speed of sound in the solution depends on the speed of sound in the undissolved crystal, the degree of electrolyte dissociation, and the number of ions formed. The information produced by measuring the speed of sound can thus be used to analyze the nature of chemical bonds. References 37: 20 Russian, 17 Western.

6508/9835

CSO: 1841/416

UDC 537.226.33

EFFECTS OF PRESSURE AND ELECTRIC FIELDS ON THE FERROELECTRIC-ANTIFERROELECTRIC PHASE BOUNDARY IN $\text{Pb}(\text{TiZr})\text{O}_3$ CERAMICS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian Vol 28, No 3, May-Jun 87 (manuscript received 5 Feb 86) pp 290-293

[Article by I. N. Polandov, O. K. Gulish, V. N. Pronin, B. I. Malyutin, A. P. Feldman and V. M. Ishchuk, Department of High Pressure Physics and Chemistry, Moscow State University]

[Abstract] A study was conducted on the ferroelectric (FE)-antiferroelectric (AFE) phase boundary relationships in the case of $\text{Pb}(\text{TiZr})\text{O}_3$ ceramics as affected by temperature and pressure. The samples under study were doped with Sn and Nb, imparting the following general formula: $\text{Pb}_{0.99}\text{Nb}_{0.02}((\text{Zr}_{0.4} - \text{Sn}_{0.6})_{1-x}\text{Ti}_x)\text{O}_{93}\text{O}_3$, where $x = 10, 12$, or 14% . Composition-temperature plots

revealed different FE-AFE phase boundary slopes for the undoped and doped samples, with a marked increase in the AFE phase with an increase in temperature. Evaluation of pressure-temperature plots up to 10 kbar showed a decrease in the FE component with an increase in pressure. However, an increase in Ti concentration from 10 to 14% was accompanied by expansion of the FE phase in the solid solutions. Phase transition increased in direct proportion to the increase in Ti^{4+} in the solid solutions. An electric field of 12-18 kV/cm was required for FE phase induction with 12% Ti, but only 2-8 kV/cm with 14% Ti. These studies demonstrated marked hysteresis with respect to temperature and pressure. Polarized ceramics with 8-14% Ti behaved as metastable systems, with a transition from the FE to the AFE phase at higher temperatures. Doping with Sn and Nb was shown to increase domain mobility. Figures 4; references 14: 6 Russian, 8 Western.

12172/9835

CSO: 1841/433

UDC 541.133:546.4/5'121-14

SPECIFIC CONDUCTIVITY OF MOLTEN SALTS $Ca_2F-CaCl_2$, SrF_2-SrCl_2 , AND BaF_2-BaCl_2

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 53, No 6, Jun 37
(manuscript received 29 Oct 85) pp 603-607

[Article by B. M. Voronin, V. D. Prisyazhnyy, E. K. Khizhnyak, V. N. Zamkov and Yu. K. Novikov, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] Conductivity measurements were made at high temperatures of the molten binary salt mixtures $Ca_2F-CaCl_2$, SrF_2-SrCl_2 , and BaF_2-BaCl_2 for optimum flux selection for electroslag welding. Over a temperature range of roughly 900 to 1500°C, log of conductivity vs. $1/T$ plots yielded smooth curves with a negative slope, demonstrating the applicability of the Arrhenius equation to conductivity estimation. Measurements of conductivity in relation to the concentration of the Cl component of the salt showed that maximum change, a decrease of ca. 1.6- to 1.7-fold, occurred at ca. 50 mole% Cl content. In terms of decreasing conductance (in $ohm^{-1} \cdot cm^{-1}$), the salts ranked as follows: CaF_2 -- 6.39, SrF_2 -- 5.67, BaF_2 -- 5.27, $CaCl_2$ -- 3.84, $SrCl_2$ -- 3.45, and $BaCl$ -- 3.15. Figures 2; references 11: 10 Russian, 1 Western.

12172/9835

CSO: 1841/430

CALCULATION OF ION-ELECTRON CONDUCTANCE OF OXIDES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 53, No 6, Jun 87
(manuscript received 20 Oct 85) pp 607-611

[Article by V. F. Zinchenko, G. A. Teterin and I. M. Minayev, Physicochemical Institute, UkSSR Academy of Sciences, Odessa]

[Abstract] A mathematical approach is proposed for differential evaluation of the contribution of ionic and electron conductance to net conductance of materials with a variety of applications, such as conductive coatings, solid electrolytes, and so forth. Combination of theoretical evaluation with experimental data for EuNbO_4 (I) and SmNbO_4 (II) over a temperature range of ca. 900 to 1200°C demonstrated the feasibility of evaluating the contribution of each component from the temperature effects. Thus, at 1200°C, the net, ionic, and electronic conductance for II were calculated at 18.0, 5.5, and $12.5 \times 10^4 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$, with an activation energy for electronic conductance of 126 kJ/mole. In the case of I, the respective values were estimated to be 5.6, 4.7, and $0.9 \times 10^4 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$, and 243 kJ/mole. Thus, the relative contributions of ionic conductance for I and II were 85 and 30%, respectively. Figures 2; references 4 (Russian).

12172/9835

CSO: 1841/430

UDC 621.315.592:527.311.322:539.213

INFLUENCE OF CuO AND Ag_2O ON ELECTRICAL CHARACTERISTICS OF BARIUM VANADATE GLASSES

Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 13, No 2, Mar-Apr 87
(manuscript received 27 Aug 85) pp 183-189

[Article by L. D. Bogomolova, M. N. Glasova, V. M. Kalygina, S. N. Spasibkina, and A. A. Khorikov, Siberian Physical-Technical Institute imeni V. D. Kuznetsov, Tomsk]

[Abstract] A detailed study is presented of the influence of CuO on the conductivity of barium vanadate glasses in both dc and ac in the 10^2 - 10^4 Hz range. The influence of Ag_2O was also studied for comparison. Measurements were performed on glasses with an initial composition of 65 mol.% V_2O_5 ·35% BaO . The introduction of CuO was found to increase conductivity in both ac and dc by decreasing the activation energy of small-radius polaron jumps due to an exchange reaction between V (IV) and Cu (II). The activation energy of the jump increases in barium vanadate glasses with Ag_2O , while conductivity decreases due to an increase in the distance between vanadium atoms. Introduction of CuO and Ag_2O does not change the nature of the polarization

process, causing no change in the concentration of dipoles and creating no new dipoles, so that ϵ'_s (static dielectric permittivity) and ϵ'_∞ (high-frequency dielectric permittivity) are independent of glass composition. Figures 2: references 19: 8 Russian, 11 Western.

6508/9835

CSO: 1841/408

UDC 537.533

CHANGES IN NKVV AUGER SPECTRA OF ZrN, NbN AND Mo₂N

Moscow POVERKHINOST: FIZIKA, KHIMIYA, MEKHANIKA in Russian No 7, Jul 87
(manuscript received 26 Aug 86) pp 86-89

[Article by Yu. M. Shulga, V. I. Rubtsov, G. L. Gutsev and Yu. G. Borodko,
Institute of Chemical Physics, Chernogolovka Branch USSR Academy of Sciences]

[Abstract] ZrN and NbN in the NaCl-type crystalline state possess a high transition temperature for transformation into a superconductive state, which is ca. 10 K for ZrN single crystals and 12-16 K for NbN films. An analysis was conducted on the shape of NKVV Auger spectra of ZrN and NbN under conditions of high resolution to assess spectral differences in relation to electronic structure and for comparison with analogous spectra of Mo₂N. The crystalline structure of Mo₂N differs from that of ZrN and NbN, but the immediate environment of the N atom in Mo₂N also represents an octahedron of metal atoms. For quantitative evaluation of the peak intensities and their positions, the spectra were transformed into Gaussian components, which revealed a low-intensity component in addition to the 6 main peaks. The low-intensity component in the low-energy portion of the spectrum presumably was related to a shake-up process. The spectral data were tabulated to provide information on the relative energies of the peaks, peak halfwidths, and relative integral intensities. Changes in the positions of the individual peaks and their halfwidths did not correlate with theoretical values based on the Lander model. Gradual changes in the NKVV spectra for ZrN, NbN, and Mo₂N caused by d-hole delocalization may explain the discrepancy. Figures 3: references 13: 3 Russian, 10 Western.

12172/9835

CSO: 1841/458a

PYROELECTRIC EFFECT ON IMAGE FORMATION OF FERROELECTRIC CRYSTALS IN SCANNING ELECTRON MICROSCOPE

Moscow POVERKHNOST: FIZIKA, KHIMIYA, MEKHANIKA in Russian No 7, Jul 87
(manuscript received 23 Oct 86) pp 125-130

[Article by N. N. Dremova, A. I. Yerko and D. V. Roshchupkin, Institute of Special Problems Technology of Microelectronics and Extremely Pure Materials, USSR Academy of Sciences, Chernogolovka]

[Abstract] A study was conducted on the effects of temperature and orientation of the substrate on the interaction of an electron probe with the surface of ferroelectric materials. The ferroelectric substrates consisted of Z-sections of LiTaO_3 crystal with a regular domain structure and a 127° angle Y'-section of LiNbO_3 crystal. The study consisted of determination of the influence of LiTaO_3 and LiNbO_3 surface charges due to the pyroelectric effect on the emission of secondary electrons and on the deflection of the primary electron beam. The orientation and temperature of the LiTaO_3 and LiNbO_3 crystals were shown to affect the contrast of the image. The formation of light and dark domain charges affected both the trajectory and the secondary emission coefficient as well as the dielectric permittivity. Figures 5; references 6: 3 Russian, 3 Western.

12172/9835

CSO: 1841/458b

UDC 666.01:539.213.1;666.22:538.614

EFFECTS OF CERIUM ON IRON-CONTAINING K-Al-B GLASS

Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 13, No 3, May-Jun 87
(manuscript received 15 Jan 86) pp 391-397

[Article by G. N. Belozerskiy, A. V. Kalyamin, E. Ye. Kornilova, G. T. Petrovskiy, and S. A. Stepanov, Leningrad State University imeni A. A. Zhdanov; State Optical Institute imeni S. I. Vavilov, Leningrad]

[Abstract] Interest in ferrites due to their magnetic and optomagnetic properties has increased with the demonstration that it is possible to grow magnetic microparticles in glass. The latter retains its transparency in the near IR region of the spectrum while acquiring the magnetic and optomagnetic characteristics of the magnetic materials. However, the magnetic phase and the disordered glass structure are known to affect the magnetic and optomagnetic properties and characteristics of the glass. The effects of different concentrations of CeO_2 on K-Al-B glasses with a constant Fe_2O_3 content were studied in relation to the Curie-Weiss law and correlated with Mössbauer spectra. Glass samples with less than 0.05 wt% CeO_2 showed low

magnetic susceptibility (2.2×10^{-6}) which followed the Curie-Weiss law over 300 to 833 K, with a Weiss constant of ca. 1000 K, and did not differ in that respect from glass without CeO_2 . Addition of 2-3 wt% CeO_2 led to deviation from the Curie-Weiss law, indicating the appearance of magnetic microparticles. Mössbauer spectroscopy indicated the formation of hematite sextets with nonequivalent positions of the Fe atoms, suggesting that regardless of the ratio of Fe_2O_3 and CeO_2 , the mixed Fe-Ce oxide (CeFeO_3) contained 90% of the Fe_2O_3 in the glass. Figures 3; references 9: 6 Russian, 3 Western.

12172/9835

CSO: 1841/458c

UDC 666.01:538.22

CONDITIONS OF MAGNETITE CRYSTALLIZATION IN GLASS AND ITS EFFECT ON ELECTROPHYSICAL PROPERTIES OF GLASS

Minsk VYESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 3, May-Jun 87 (manuscript received 17 Dec 84) pp 116-118

[Article by V. V. Tavgen, Ye. V. Shpak and L. G. Khodskiy, Institute of General and Inorganic Chemistry, ESSR Academy of Sciences]

[Abstract] Studies with $(72.5 - x)\text{SiO}_2 \cdot 10\text{Al}_2\text{O}_3 \cdot 17.5\text{RO} \cdot x\text{Fe}_2\text{O}_3$ glasses demonstrated that magnetite was formed when the glass was synthesized at 1500°C with more than 10 mole% iron oxides. X-ray analysis failed to reveal magnetite when iron oxide concentration was below 10 mole%. However, in the latter case, specific magnetization suggested the formation of small concentrations of magnetite, a fact confirmed by optical microscopy. Magnetite in glass samples formed with 10 mole% or more iron oxide imparted an electrical conductivity of ca. 125 ohm-cm, which increased exponentially with an increase in temperature during which the activation energy was 0.1-0.2 eV. The specific magnetization increased from less than 5 to ca. $20 \text{ A}\cdot\text{m}^2/\text{kg}$ in going from an iron oxide concentration of 7.5 to 17.5 mole%. The concentration of resultant Fe_3O_4 was directly correlated with magnetization. The resultant increase in conductance, by 2 to 3 orders of magnitude, was accompanied by a decrease in the activation energy for conductivity from ca. 1.6 to ca. 0.3 eV. The concentration of magnetite was dependent on the method of melt cooling. Rapid cooling with water of a melt containing 12.5 mole% iron oxide resulted in a specific magnetization of $3 \text{ A}\cdot\text{m}^2/\text{kg}$, while cooling on a metallic plate gave a magnetization value of $15 \text{ A}\cdot\text{m}^2/\text{kg}$. Figure 1; references 8: 1 Belorussian, 7 Russian, 1 Western.

12172/9835

CSO: 1841/458d

THERMAL STABILITY OF ALKALI-METAL HEXAFLUOROXENATES (IV)

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 295, No 2, Jul 87
(manuscript received 27 Jan 87) pp 378-381

[Article by Yu. M. Kiselev, N. Ye. Fadeyeva, A. I. Popov, M. V. Korobov,
V. V. Nikulin and Academician V. I. Spitsyn, Moscow State University
imeni M. V. Lomonosov]

[Abstract] A mass-spectrometric study was conducted on the thermal stability of alkali-metal hexafluoroxenates (IV) (M_2XeF_6 , $M = Na, K, Rb, Cs$). The study, over a temperature range of 20-600°C with 10^{-2} to 10^{-1} mm granules, led to determination of the maximum temperature of decomposition (T_g), temperature range of decomposition (ΔT), and the activation energies E_a . These parameters changed in the Na to Cs series in a manner indicating that an increase in the size of the cation favored stability of the hexa-fluoroxenates (IV). Combination of thermoanalytic data with mass-spectrometric findings showed that, on heating, the compounds decomposed according to the following equation: $M_2XeF_6 \rightarrow 2MF + XeF_4$. The XeF_4 underwent partial dissociation into XeF_2 and F_2 . The T_g values of 215-570°C demonstrated that the hexafluoroxenates (IV) were thermally as stable as the octafluoroxenates (VI). References 8: 5 Russian, 3 Western.

12172/9835

CSO: 1841/454a

UDC 621.373.826

PRE-THRESHOLD DESTRUCTION OF POLYMETHYLMETHACRYLATE UNDER ACTION OF LASER IRRADIATION

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 5, May 87
(manuscript received 25 Jul 86) pp 707-709

[Article by A. M. Kondyrev, O. F. Pozdnyakov, A. Ye. Chmel and V. S. Yudin, Physical-Technical Institute imeni A. F. Ioffe, USSR Academy of Sciences, Leningrad]

[Abstract] Experience has shown that transport polymers are definitely affected by cumulative action of IR or visible laser radiation; sample "destruction" may be achieved by a single pulse with energy density Q^* or by repeated irradiation with $Q < Q^*$. Studying this is difficult because the breakdown products of amorphous polymers, which are highly prospective organic materials for laser technology, are low-molecular-weight volatile substances requiring low inertia methods for their adequate registration during the pulse action. Processes were studied occurring during interaction of pulsed IR irradiation with polymethylmethacrylate (PMMA) using a mass spectroscopic method which can register volatile products directly during irradiation. When sufficient energy was used, intensive breakdown of PMMA was observed. A level was determined $Q < Q^*$ at which a single pulse showed no volatile products. When $Q = 0.5 Q^*$, only after 30 impulses was the breakdown of PMMA observed. With the $Q = 0.5 Q^*$ dose, one pulse, of duration of $8 \cdot 10^{-4}$ sec, generated on the average 10^6 - 10^7 chain breaks. Heating the irradiated sample showed no formation of MMA, i.e., the radicals disappeared at the moment of macrodestruction. Figures 2; references 8 (Russian) (1 by Western authors).

7813/9835
CSO: 1841/414

THERMOOPTICAL CYCLES DURING RESONANCE PUMPING OF CARBON MONOXIDE

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 5, May 87
(manuscript received 4 Jun 86) pp 609-614

[Article by V. M. Shmelev and A. D. Margolin Institute of Chemical
Physics, USSR Academy of Sciences, Moscow]

[Abstract] Two types of critical phenomena occur during resonance illumination of molecular gas: optical and heat instability. Development of optical instability with steady gas temperature input is due to a nonlinear rate of optical excitation of molecules as a function of the magnitude of nonequilibrium vibrational energy of the system. The goal of the present study was to calculate the excitation of vibrational degrees of freedom of molecular gas under nonisothermal conditions by means of optical illuminator, which illustrates the potential of forming the so-called thermooptical cycles. The kinetics of intermolecular exchange and the reaction of illumination with gas is described by the model of harmonic oscillation. The following thermooptical regimens were found in the system after solving proper equations: heat transillumination of gas, "darkening" of the medium, and thermooptical vibrations. Thus, based on the quantitative method, thermooptical vibrations. Thus, based on the quantitative method, thermooptical cycles were observed in carbon monoxide exposed to steady resonance optical pumping and heat removal. A range of initial parameters was found at which an autovibrational process develops in the system, expressed by periodic "lightening" and "darkening" of the medium. Figures 4; references 8: 7 Russian, 1 Western.

7813/9835
CSO: 1841/414

UDC 666.11.01:539.231.1

CRYSTALLIZATION OF GLASSES IN SYSTEM ZrF_4 - BaF_2 - LaF_3 - NaF

Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 13, No 2, Mar-Apr 87
(manuscript received 12 Sep 85) pp 163-167

[Article by V. B. Kalinin, Ye. G. Grechko, V. N. Sigayev, V. V. Sakharov,
A. Yu. Shashkov and T. V. Semenova]

[Abstract] A study was made of the sequence of formation of crystalline phases in fluoride glasses in the system ZrF_4 - BaF_2 - LaF_3 - NaF . This system is characterized by a wide transmission range in the UV, visible, and near IR regions of the spectrum, low values of theoretical loss in the wavelength region 2-4 micrometers (10^{-2} - 10^{-3} dB/km), high chemical stability at the low temperatures of softening and melting, and zero material dispersion in the wavelength region 1.6-1.7 micrometers. Above all, fluoride glasses, containing

rare earth elements, exhibit fluorescent activity. Phases were identified on a diffractometer using specimens obtained in the process of differential thermal analysis. The glasses were synthesized from fluorides of zirconium, barium, sodium, and lanthanum in platinum crucibles in a platinum chamber sealed with a platinum cover in a helium medium. The maximum glass-making temperature was 850°C, and the time, one hour. It was found that crystallization occurs in two or three stages; increasing the content of NaF reduces both glass point and crystallization temperature. The crystalline phases exist in narrow temperature intervals. The first crystalline phase is the most symmetrical cubic γ -ZrF₄, which is related to the maximum approximation of local cubic phase symmetry to glass symmetry. The phase composition of the partially crystallized glasses in all stages of heat treatment is related to the structure of the fluoride glasses. Figure 1; references 10: 5 Russian, 5 Western.

6508/9835
CSO: 1841/408

UDC 666.266

MATHEMATICAL MODELING OF FORMATION OF COLOR CENTERS IN HETEROGENEOUS PHOTOCHROMIC GLASSES

Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 13, No 2, Mar-Apr 87
(manuscript received 24 Jun 85) pp 196-201

[Article by A. V. Dotsenko, A. V. Morozov and V. A. Tsekhomskiy]

[Abstract] Photochromic glasses are under active study as integrated optical elements: modulators, gates, and laser radiation switches, including switches for pulsed laser radiation. This article studies a simplified model, describing the kinetics of darkening of photochromic glasses upon exposure to light by reducing the processes of seed formation and growth into two basic stages. In the first or seed-formation stage of photolysis, atomic silver is separated on the surface of AgHal microcrystals; then, due to diffusion of mobile silver atoms, random formation of fluctuating silver aggregates occurs, so that radiation not only results in segregation of atomic silver, but also stabilization of fluctuating aggregates or "seizing." Differential equations are presented to describe the change in concentration of color centers and seeds. Analysis of the equations' solution can explain the more important peculiarities in the kinetics of darkening of heterogeneous photochromic glasses, including the presence of an induction period, dependence of activation on intensity, and deviation from the interchangeability rule. Figures 2; references 24: 16 Russian, 8 Western.

6508/9835
CSO: 1841/408

EFFECTS OF LiI ON ASSOCIATION OF RHODAMINE 6G MOLECULES IN ISOPROPANOL-CCl₄ MIXTURES

Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 23, No 3, May-Jun 87 (manuscript received 28 Oct 85; in final form 30 Jan 87) pp 368-372

[Article by A. M. Saletskiy, V. A. Shekunov and V. I. Yuzhakov, Moscow State University]

[Abstract] Interest in studying the effects of salts on the association process of molecules in solutions is due to the fact that solutions of dyes with electrolytes are widely used in various electroluminescent and laser systems. Fluorescence polarization studies were conducted on the association parameters of rhodamine 6G in amixture of isopropanol and CCl₄, with subsequent evaluation of the effects of LiI on the association process. Addition of CCl₄ led to a concentration-dependent reduction in absorption at 532 nm, with the concomitant appearance of a strong absorption at ca. 510 nm due to association of dye molecules into complexes. Addition of LiI to a solution containing 96 vol% CCl₄, ensuring maximum complex formation, resulted in breakdown of the rhodamine 6G complexes into monomers. The enthalpy for dimer formation increased from 7.5 kJ/mole to 11.3 kJ/mole in going from 0 to 3×10^{-4} M LiI, pointing to a change in the solvate envelope of the dye molecule complexes. The latter resulted in a change in the geometrical features of the dye complexes, as indicated by a decrease in their volume and an increase in the asphericity coefficient. Figures 2; tables 1; references 22: 21 Russian, 1 Western.

12172/9835

CSO: 1841/454b

UDC 541.49

SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF TRI-NUCLEAR COPPER (II)
BIS(HEXAFLUOROACETYLACETONATE) WITH NITROXYL RADICAL OF 4-PHENYL-2,2,5,5-
TETRAMETHYL-3-IMIDAZOLINE-1-OXYL

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 32, No 6, Jun 87
(manuscript received 10 Oct 85) pp 1403-1406

[Article by V. I. Ovcharenko, V. N. Ikorskiy, N. V. Podberezskaya,
N. V. Pervukhina and S. V. Larionov, Institute of Inorganic Chemistry,
Siberian Department, USSR Academy of Sciences]

[Abstract] Coordination of the $N\dot{O}$ fragment by a metal ion containing an unpaired electron results in exchange reactions of a strong antiferromagnetic or weak ferromagnetic type, the latter case being of great interest, since ferromagnetic exchange reactions occur over rather short distances between the copper and nitroxyl fragment oxygen atoms with significant flexure of the Cu-O-N angle. The authors synthesized and studied coordination compounds of copper bis(hexafluoroacetylacetonate) with various ligands and nitroxyl radicals of the imidazoline series 4-phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl (L). Reactions of $Cu(hfacac)_2 \cdot 2 H_2O$ with L always resulted in precipitation of a solid phase with the composition $Cu(hfacac)_2 \cdot 2/3 L$. The stoichiometric composition of the compound was retained upon recrystallization, indicating good stability of the solid phase, which quantitatively sublimated at 100-120°C. X-ray structural studies of single crystals of the solid were performed, indicating a molecular-island structure with structural units consisting of a tri-nuclear molecule $[3 Cu(hfacac)_2 \cdot 2 L]$, consisting of three $Cu(hfacac)_2$ bischelates connected by two bidentate-bridges of L. Data on the structure indicate the presence of a three-center exchange-bonded cluster $N\dot{O}-Cu^{2+}-O\dot{N}$ and quasi-isolated "terminal" Cu^{2+} ions. The ferromagnetic exchange reaction occurs both within the exchange cluster and between individual molecules. Figures 2; references 9: 4 Russian, 5 Western.

6508/9835
CSO: 1841/419

UDC 631.244.2

ORGANIZATION OF REPAIR OF CHEMICAL PRODUCT STORAGE AREAS

Moscow KHIMIYA V SELSKOM KHOZYAYSTVE in Russian No 6, Jun 87 pp 42-44

[Article by M. T. Mironov and M. S. Dylkov, candidates of technical sciences, I. V. Stepanov and V. M. Lapshina, All-Union Scientific Research and Design Institute for Technology and Economics of Storage, Transportation, and Mechanization of Application of Mineral Fertilizers, and V. A. Petrov, All-Union Scientific-Production Association "Soyuzselkhozkhimiya"]

[Abstract] Repair of chemical storage facilities used for mineral fertilizers, chemical agents for protection of plants and other products is a difficult task due to their height (up to 26 m) and exposure of the constructed structures to the chemicals themselves, precipitation, and atmospheric pollution. In 1982, the Dzerzhinsk Rayon "Selkhozkhimiya" Association in Minsk Oblast created a special self-financing construction and repair section for the repair of such structures, consisting of 45 persons performing 500,000 rubles worth of repair work each year. The section is able to perform various types of work since each worker has two or three specialties. Repair organizations in other areas have followed suit, leading to increased productivity and financial savings, which are particularly important because some 30% of chemical storage facilities need major repairs.

6508/9835
CSO: 1841/437

ALTERNATIVE TO PESTICIDES

Moscow ENERGIYA in Russian No 6, Jun 87 pp 38-43

[Article by Yevgeniy Gol'tsman, correspondent]

[Abstract] This article reports on an interview with Yu. T. Kalinin, Deputy Minister of the Medical and Microbiological Industry, M. V. Gorlenko, corresponding member of the USSR Academy of Sciences, Academician V. A. Tikhonov, All-Union Agricultural Scientific Research Institute, V. D. Zybin, Director, Production-Technical Administration, "Biopreparat" Main Administration of the

Ministry of the Medical and Microbiological Industry, Doctor of Chemical Sciences A. M. Moiseyenko, and Candidate of Biological Sciences G. A. Zakladnyy on the subject of safe alternatives to pesticides. Each year, tremendous funds are expended in the development and manufacture of new pesticides, while the laboratories studying biological alternatives to pesticides can be counted on one hand. Selective, non-toxic, synthetic pyrethroids are now being developed to replace traditional broad-spectrum pesticides. Substances such as bitoxibicillin are now in production which can replace traditional pesticides in many areas. Even today, the quantities of pesticides used could be greatly reduced. Excessive use of pesticides is an indication of unsophisticated agricultural techniques. Previous problems such as short shelf-life and poor solubility of biological plant protection substances have now been solved. The advent of viral preparations for plant protection is eagerly awaited but must await development of economical full-scale production methods. Major hindrances to the introduction of alternatives to pesticides include the difficulties of industrial production of alternatives and organizational obstacles: the synthesis of new preparations, testing, and development of methods for industrial production all occur in different departments, with specialists not being in touch with each other.

6508/9835

CSO: 1841/437

PETROLEUM, COAL PROCESSING

CONVERSION TO NATURAL GAS FUEL FOR MOTOR VEHICLES IN RSFSR

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 29 Apr 87 p 2

[Article by R. Khadzhiyev under the "Courier of the Scientific and Technical Organization" rubric: "Gas Instead of Gasoline"]

[Text] The soviet of the Scientific and Technical Organization of the RSFSR Ministry of Motor Transport actively participates in the conversion of motor vehicles, enabling them to use compressed natural gas as fuel. Thousands of gas cylinder motor vehicles are now in use in the RSFSR.

By considering that conversion of diesel motor vehicles to use gas as power fuel is one of the quickest ways to economize petroleum fuel, specialists of the Central Board of the Scientific and Technical Organization of Motor Vehicle Transport and IAMI [as published] conducted operational tests of KamAz brand gas-diesel motor vehicles. Good results were obtained.

17410/9835

CSO: 1841/361

ACCELERATION IN POLYMER MACHINE BUILDING INDUSTRY

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 25 Jun 1987, p 3

[Article by V. Dementyev, secretary of the Yaroslavl Polymer Machine Building Scientific Production Association Party Committee, Yaroslavl: "Acceleration--Not from Nothing"]

[Text] The minister visited us at the Yaroslavl Polymer Machine Building Plant a little more than three years ago. And a critical letter from workers which was sent to the editor of SOTSIALISTICHESKAYA INDUSTRIYA served as the reason for the visit. The minister spent two days getting acquainted with the enterprise: he literally examined every corner, sought advice from the workers, and consulted with designer specialists and workers of the ministry. The problems of the collective were also discussed in detail in the oblast committee of the party. The minister met with the authors of the letter only after he had personally looked into the state of things. You agree that the minister goes to the place and personally investigates far from every letter. Therefore, this conversation was remembered precisely by its participants.

"First of all," said the minister, "I am grateful to you for the justified criticism. Your letter is clear evidence of how the Law of the Worker Collectives, an example of the participation of workers in the national economy, has been translated into life. What impression do I have from acquaintance with the plant? I shall tell you openly that I am dissatisfied with the work in your enterprise. Completion of restructuring is as necessary as air for your plant. I am personally convinced of this, and I shall try, as minister, to convince the leaders of the corresponding agencies and departments."

Exhaustive measures of help for the enterprise were specified in the minister's order. Unfortunately, they also remained thus on paper. Such a fate also befell the extensive measures developed for the 70th anniversary of the plant and approved by the minister and also by the first secretary of the CPSU oblast committee and by the president of the oblast executive committee. The coming of the minister, his meetings, and assurance of help raised hope for changes in the collective. The collective, as they say, took heart. The high rates of growth of the volumes of production specified in the 12th Five-Year Plan also did not disturb us, because they were reinforced by the corresponding plans for the restructuring of the enterprise and for social and

cultural development. On a wave of enthusiasm and fervor, the collective accomplished, it would seem, the impossible: in two years, actually with a lowering of the volumes of technical reequipment, the output of production was increased almost by 30 percent. This shows what the human factor is!

But, alas, enthusiasm in the collective has noticeably dropped today. Together with fervor in the workers and specialists, pessimistic moods are becoming more and more apparent. And the fault of this is the failure of the program drawn up according to the results of the minister's visit. The speech of the minister proved to have superficial verification. The measures which he specified both in the production and in the social spheres were not fulfilled. A third of the area of the plant has been allocated to repair buildings, and 40 percent of the equipment is completely worn out. On such equipment, yes, even under conditions of state acceptance, we must achieve in the current year a nine percent growth in production volume! And this is in addition to the 30 percent obtained in the previous two years.

Still higher rates are planned for the plant in the following years of the Five-Year Plan--10 to 11 percent. And they are not made up. The Five-Year Plan is assigned, taking into account the accomplishment of restructuring and technical reequipment of the enterprise. But the minister, who recognized the unsatisfactory work of the ministry on the given problem, resigned. And here, indeed, all the decisions which he signed for the plant automatically were rescinded in the second plan.

We knocked at the door of the ministry's cabinets, we argue, we remind them of old and recent documents, we speak about the situation being more complex, and they answer us that, they say, they know all this, but it is necessary to begin all over again. But the conversation does not lead to any succession of decisions.

How is that? We understand that other people have come, but their real duty is not to discard the correct decisions of the previous leadership and to consider the obligations given by them earlier, all the more when one refers to decisions of the sector headquarters. They were not prepared, however, by just one important person, but in our case, they were developed by a group of competent specialists. It is impossible to cancel the answer found and to send them to the archives only because they were signed by former leaders.

Unfortunately, we encounter such an attitude not only in the Ministry of Chemical and Petroleum Machine Building. The leadership in the oblast committee, in the oblast executive committee, and in the Glavverkhnevolgstroy [as published] has been relieved over the past three and a little more years. And they are working with us everywhere from a clean slate: everywhere we have to prove what we had already proved long ago and to waste time on discussions instead of doing the work. And this immediately slows us down. This means that restructuring is also slowed down for us. If, for example, the ministry to a high degree is guilty of the disruption of plans for restructuring, the underfulfillment of the social program has taken place basically because of lack of attention of local agencies to this problem. Thus, the ministry allotted two million rubles to the plant society as promised. And only 15 percent of this was appropriated due to the fault of

the city executive committee.

Timely replacement of the leaders, in our opinion, is effected in order not to lose time. It is necessary in order to make up for the lost years. And we have other leaders who see their start in a slowed variant, as if for a new appointment someone has relaxed the period for adaptation in an armchair and in an office rocker. Thus one can only move backwards. We are certain that such a leadership style does not correspond to the spirit of the times.

12410

CSO: 8144/4318

COMBINED PRESSURE AND SHEAR STRAIN IN POLYMER AND RUBBER PRODUCTION

Moscow KRASNAYA ZVEZDA in Russian 28 Mar 87 p 4

[Article by Academician N. Yenikolopov and Doctor of Technical Sciences M. Fridman, "'The Fourth Whale' in Chemistry of Astonishing Opportunities Promised by a New Production Process"]

[Text] Man has been striving to get the most out of the fruits of nature since time immemorial. He learned how to make paper from reeds, brick and pottery from clay, metal from ores, and glass from sand. He even made extensive use of natural polymers--rubber, timber, various resins--for his needs.

Chemistry became his reliable ally. New materials created the preconditions for truly revolutionary changes in the most varied sectors of industry, science and technology, and in our very way of life. In turn, this confronted scientists working with high-molecular compounds with even more complex problems. Great hopes are today being pinned on solid state chemistry, which represents a radical departure in the development of polymer chemistry.

As far back as the Middle Ages, alchemists already recognized that heat and mass transfer were needed for any transformation of matter to take place. In addition, these transformations occur at a higher rate in low-viscosity media--gases and liquids. Ancient times also saw the formulation of a far-reaching technological concept according to which it was better to mix substances and conduct chemical reactions in gaseous or liquid phases. Names were also given to the "three whales"--the three major factors affecting the intensity of a chemical reaction--temperature, pressure and catalysts.

Solid state technology did not capture the attention of chemists and was not considered all that promising. Against all things "obvious" and "doubtless," however, research has recently demonstrated that various chemical reactions can also occur in solids under certain conditions. The scientists were amazed at the rate of these reactions. But let us start at the beginning.

About three years ago, a discovery registered into the State Register under the number 288 was made in the country. Its authors managed to discover "the fourth whale" in chemistry, establishing that high pressure coupled with shear strain stimulates the polymerization of low-molecular substances--monomers.

These substances gave rise to over 100 new names, among which are the aromatic hydrocarbons (benzene, naphthalene, stilbene, and so on). And here is the interesting part: None of them is able to change into a polymer under conditions of conventional chemical technology.

Amazing transformations set in when an initial material preliminarily compressed at a pressure of 10 to 100 kilobars is subjected to torque strain (100 to 1000 degrees). Just what happens during this?

We should make clear immediately that no heating of material is involved here at all. Calculations and measurements show that the temperature of the medium increases slightly and that there are no "hot" spots in this case. In addition, solid-phase reactions reveal a "capricious" nature as far as temperature is concerned because their rates are entirely independent of temperature. As chemists like to say in cases such as this, the activation energy--the measure of self-acceleration of the process as temperature increases--is virtually equal to zero.

In short, physicochemical processes in solids in practice take place at a uniform rate both at elevated and very low temperatures while exposed to high pressure and strain.

The major conclusion arrived at by scientists as a result of numerous experiments is that a substance subjected to torque and shear strain becomes entrained in a so-called plastic flow with its particles acquiring a special "supermobility".

Super-fast polymerization is carried out in an anvil-type apparatus which works on the principle where the compression of a solid sample (if sufficiently thin) between two surfaces does not result in the outflow of substance. The solid is placed between anvils made out of bearing steel or another hard alloy and shaped like truncated cones. A press is used to compress the substance in such a way as to create a pressure of up to tens or even hundreds of kilobars, after which one of the anvils is shifted relatively to the other (shear strain comes about in the substance).

Theoretical foundations for a new technology have now been developed. While it is true that much remains to be rendered more precise, studied in greater detail, and checked, scientists are answering the question of whether production processes can be developed on these foundations. Also in the planning stage are continuous-operation industrial installations--solid reactors. One of the variants will consist of units similar to extruders, which are used extensively at present for melting polymers and extruding them through forming devices during the manufacture of sheets, pipes and other formed articles.

The advantages of the new technology are obvious: Increased labor productivity, simplified design of equipment, the complete elimination of thinners from the production process, and ecological purity. Finally, there is the possibility of producing new materials with unique properties. Shear processing of filled polymers or different mixtures of polymers at a high pressure results in synthetic materials of exceptionally high uniformity, transparency, and strength.

Of great importance from a scientific and practical standpoint, as well, is another direction: using the principle of pressure processing materials while subjecting them to shear strain for mixing and reducing them. The "super-mobility" phenomenon of particles in solids has made it possible to find a new approach to obtaining mixtures of polymer materials.

Hard organic solids and metals are mixed in special devices at velocities hundreds and thousands times higher than the velocity at which solids penetrate one another while being mixed in a conventional manner. This phenomenon made it possible to carry out an entire sequence of solid-phase processes at room temperature. Numerous molecular solutions were obtained, including mixtures of iron with nickel and copper, nickel and titanium, different complexes of iron and graphite, porphyrin and salts, ferrocene and graphite, as well as mutually inert polymers (such as polyethylene mixed with polypropylene, polystyrene, and cellulose, polyvinylchloride mixed with cellulose, and polyethyleneterephthalate mixed with polystyrene).

Scientists suggested yet another interesting method which can be applied in practice. Involved here is a radical new energy conserving technology for reducing polymers.

Here, traditional technology was based on two basic physical effects: impact load and cutting. Existing crushing machines and pulverizers are distinguished by high energy-consumption and low efficiency (often less than 1%). The process of grinding to a fine powder is very labor-consuming for several substances (e.g., rubber, synthetic rubber, and polyethylene). It can only be carried out if the substances are frozen at very low temperatures (cryogenic technology).

The new process for grinding different materials suggested by Soviet researchers may be termed the elastic-deformation method. The technology is relatively easy to carry over to the existing industrial base. Extrusion machines employed in the chemical industry can in principle be used for this purpose. In these devices, the polymer material is subjected to pressure and shear strain while the screw conveyor rotates.

Under specific temperature-force conditions, the initial raw material is loaded into the screw conveyor, in the form of lumps, granules, crumbs, bands, and fibrous materials and comes out as a finely dispersed powder, or "flour" (particle sizes range from 10 to 500 microns). The process can be optimized for different materials and the dispersion of the product adjusted by varying the speed of the working heads, temperatures in different parts of the machine, and other parameters.

Experimental studies of polymer mixtures have revealed yet another unusual fact: materials which by themselves are not pulverized by the extruders break down into powders if another polymer is added to them. Some examples of this are high density polyethylene, which is pulverized in a mixture with polypropylene, and cellulose, if a small quantity of polyvinylchloride is added to it. These processes can be called "co-pulverization".

The new pulverizing technology makes it possible using industrial equipment to produce such valuable materials as wood flour, rubber crumb, and thermoplastic, cellulose, and rubber powders. It becomes possible to reduce two or even several materials at one time, as well as to obtain compositions during a combined "pulverizing-mixing" process. The new technology is distinguished by relatively low energy consumption and a high production rate.

Experiments and industrial practice relating to pulverizing rubber waste products have also demonstrated that the process is characterized by relatively low energy consumption and high productivity. Substances can be processed via the "pressure plus shear strain" procedure not only in extruders, but in milling machines as well.

Scientists still have a lot of work ahead of them with respect to uncovering and exhaustively studying the mechanisms and patterns underlying solid state chemistry as well as to determining the optimum conditions for the processes and implementation of equipment. Even so, we may safely hope that solid state chemistry will in the very near future become incorporated into the economy on a large scale and help to accelerate technological progress. In short, a lot is expected from solid state chemistry.

13126/9835

CSO: 1841/399

JOURNAL ISSUE ON LIQUID RUBBERS

Moscow KHIMIYA: ZHIDKIYE KAUCHUKI in Russian No 4, Apr 87, pp 1-2

[Table of contents and annotation from journal issue "Liquid Rubbers" by Doctor of Chemical Sciences Aleksandr Ivanovich Krashennikov and Candidate of Chemical Sciences Vladimir Petrovich Shoboldin, Znaniye, 32 pages]

[Excerpt] TABLE OF CONTENTS

| | |
|---|----|
| Introduction..... | 3 |
| Methods for Synthesizing Low-Molecular-Weight Polymers..... | 3 |
| Behavior of Low-Molecular-Weight Polymers and Their Solutions..... | 7 |
| Rheological Properties of Oligomers..... | 11 |
| Methods for Vulcanizing Liquid Rubbers..... | 14 |
| Areas for Using Synthetic Liquid Rubbers in Anti-Corrosion Practice.. | 25 |
| Conclusion..... | 29 |
| Literature..... | 31 |

ANNOTATION

In recent years, interest has risen in low-molecular-weight polymers--liquid rubbers which can be used successfully in different sectors of the national economy. In connection with this, active searches for methods for synthesizing these polymers are being conducted, and their structure, the properties of dilute and concentrated solutions, vulcanization methods (by traditional curing methods and with mineral salts of transition metals), and areas for using materials based on them are studied.

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INFLUENCE OF PRELIMINARY LASER IRRADIATION ON PROCESSES OF THERMAL OXIDATIVE DESTRUCTION OF POLYACRYLONITRILE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 29, No 5, May 87
(manuscript received 10 Nov 85) pp 982-987

[Article by I. B. Klimenko, N. V. Platonova, V. I. Grachev, B. A. Vinogradov and V. R. Arbuzov, Leningrad Institute of the Textile and Light Industry imeni S. M. Kirov]

[Abstract] The purpose of this work was to clarify the influence of laser radiation on the formation of polyconjugate structures in chains of polyacrylonitrile macromolecules with subsequent heat treatment. Processes of thermal oxidative destruction were studied by IR and electron spectroscopy. Laser irradiation was found to form polyconjugate structures which continued to develop during heat treatment. A new band appeared in the spectrum of the polymer powder close to the laser radiation frequency. The new band disappeared after subsequent heat treatment. The intensity of the broad band with a maximum at 1600 cm^{-2} increased with increasing heating time. Laser radiation was found to bond molecules of DMFA (dimethylformamide) to the polyacrylonitrile films, influencing thermal oxidative destruction processes. Figures 5; references 10: 9 Russian, 1 Western.

6508/9835
CSO: 1841/415

UDC 541.64:535.3

ELECTRO-OPTICAL EFFECTS IN COMB-LIKE LIQUID CRYSTALLINE POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 29, No 5, May 87
(manuscript received 25 Nov 85) pp 1037-1043

[Article by I. A. Korobeynikova, R. V. Talroze, V. P. Shibayev, and N. A. Plate, Moscow State University imeni M. V. Lomonosov]

[Abstract] Substances in the liquid-crystal state can undergo structural changes under the influence of electrical and magnetic fields. Changes in

liquid-crystal-polymer orientation cause changes in optical properties of polymer films. This article studies in detail the influence of an electrical field on certain cholesteric polymers to determine the basic principles of their electro-optical behavior and find the analogies and differences between polymer and low-molecular-weight liquid crystals. An alternating electric field was used to produce texture transformations and unwind cholesteric spirals in comb-like cholesteric acrylic polymers. The structural transforms observed were qualitatively similar to electro-optical effects observed for nematocholesteric low-molecular-weight mixtures. The specific structural and kinetic properties of the reorientation process observed resulted primarily from the chain structure of the macromolecules and spiral ordering of the polymer liquid crystal. Figures 6; references 8: 6 Russian, 2 Western.

6508/9835

CSO: 1841/415

UDC 541.64:535.557

PRE-TRANSITIONAL PHENOMENA AND ELECTRICAL BIREFRINGENCE IN ISOTROPIC PHASE OF LIQUID CRYSTALLINE POLYMER WITH MESOGENIC GROUPS IN SIDE CHAIN

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 29, No 5, May 87
(manuscript received 5 Dec 85) pp 1091-1096

[Article by Ye. I. Ryumtsev, M. A. Agafonov and V. N. Tsvetkov, Scientific Research Institute of Physics, Leningrad State University imeni A. A. Zhdanov]

[Abstract] A study is made of the Kerr effect in the isotropic phase of a comb-like polyacrylic polymer with mesogenic side chains. The method used allows study of the kinetics of dipole orientation in the polymer and the monomer at the molecular level. Relaxation phenomena are observed, similar in their nature to the pre-transition effects in low-molecular-weight liquid crystal compounds. Comparison of the electro-optical properties of the polymer with low-molecular-weight compounds indicates that polymer chain movement is responsible for the electrical birefringence observed. Figures 6; references 15: 10 Russian, 5 Western.

6508/9835

CSO: 1841/415

ANOMALOUS MICROSCOPIC ETCHING OF NITROCELLULOSE DETECTOR FILMS

Moscow PLASTICHESKIYE MASSY in Russian No 5, May 87 p 61

[Article by S. V. Stovbun, A. G. Salina, A. I. Kuzayev, and A. I. Mikhaylov]

[Abstract] Plastic track detectors based on cellulose nitrate are highly sensitive to nuclear radiation and are widely used in various branches of technology. Methods of gel-penetrating chromatography, optical microscopy and chemical etching were used to study the microstructure with anomalous etching and analyze its relationship with molecular-weight distribution heterogeneity in the initial cellulose nitrate medium. The variation in background defect density of a cellulose nitrate detector as a function of the molecular-dynamic constant spectrum of the polymer can be used to test the resolution of a film by molecular-weight distribution studies of the cellulose nitrate raw material, allowing detector parameters to be controlled. References 4 (Russian).

6508/9835

CSO: 1841/415

UDC 541.64

RADIATION-CHEMICAL OXIDATION OF POLYETHYLENE: INFLUENCE OF DOSE RATE ON MECHANICAL PROPERTIES

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 21, No 3, May-Jun 87
(manuscript received 10 Dec 85) pp 219-224

[Article by A. A. Dalinkevich, S. G. Kiryushkin, F. V. Shemarov, and Yu. A. Shlyapnikov, Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] A study is made of the relationship between conditions of radiation-chemical oxidation and mechanical properties of polyethylene. Studies were performed on nonstabilized low density polyethylene with a molecular weight of 120,000 and a degree of crystallization of 42%. Extruded films 85 μm thick were irradiated in air at room temperature with ^{60}Co γ -radiation or accelerated electrons with $E = 0.7$ MeV. The γ -radiation dose rate was 0.3-9.6 Gr/s and the electron dose rate 200-10⁴ Gr/s. Changes in mechanical properties of the polymer and the concentration of carbonyl groups formed were related linearly, although the linear relationship was disrupted if the process was limited by diffusion of oxygen within the specimen. Figures 4; references 12: 9 Russian, 3 Western.

6508/9835

CSO: 1841/416

MOBILITY OF CHARGE CARRIERS IN POLYOLEFINS

Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 21, No 3, May-Jun 87
(manuscript received 24 Jun 85) pp 241-245

[Article by V. N. Abramov, A. P. Tyutnev, Ye. D. Pozhidayev, V. S. Sayenko, A. V. Vannikov, V. V. Filippov and V. G. Nikolskiy, Moscow Institute of Electronic Machine Building; Institute of Electrochemistry imeni A. N. Frumkin, USSR Academy of Sciences; Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] Results are presented from a study of the mobility of charge carriers in high density polyethylene, polypropylene, and polystyrene films over a broad temperature interval with various values of flight-of-time external electric field strength. The flight-of-time method was supplemented by experiments on radiation conductivity for nanosecond and microsecond exposures. Drift mobility was measured by the flight-of-time method with a electron beam energy of 4.7 keV in a vacuum of $3 \cdot 10^{-3}$ Pa at 18-120°C. The behavior of charge carriers in the polyolefins was found to vary. The variation of drift mobility as a function of temperature indicated that a gaussian distribution of traps controls the transfer of charge carriers and that the exponential distribution of traps in high pressure polyethylene extends to a depth corresponding to a charge carrier discharge time of about 10^{-2} s at 300 K, after which it is sharply cut off. Figures 4; references 12: 10 Russian, 2 Western.

6508/9835
CSO: 1841/416

UDC 621.357.53; 678.029.06

METALLIZATION OF POLYMER COMPOSITION BASED ON POLYPHENYLENE OXIDE

Vilnius TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B in Russian No 2, Mar-Apr 87 (manuscript received 11 Dec 85) pp 50-56

[Article by R. E. Ramanauskas, S. A. Barankov, E. L. Matulenys and M. I. Shalkauskas, Institute of Chemistry and Chemical Technology, LSSR Academy of Sciences]

[Abstract] The purpose of this work was to find a method to modify the surface of a polyphenylene-oxide-based polymer composition to provide the maximum bond strength with copper. Studies were performed with dielectric plates made of polyphenylene oxide 1 mm thick, produced on hydraulic presses. The composition was 54% PFO, 40% TiO₂, and 6% copolymer of styrene with α -methyl styrene. The surface was etched with various chromate-sulfate mixtures. Electron microscopic studies of the surface indicated that one reason for poor bonding might be insufficient roughness of the polymer surface, the presence of significant amounts of TiO₂ on the surface, and the natural layered

structure of the polymer. A firm bond can be achieved by etching a rougher surface on the polymer and removing the weakly-bonded TiO_2 filler particles. The greatest strength is achieved by etching the polymer for two to three minutes at 40°C in a solution containing 4.2 mol/l CrO_3 and 3.8 mol/l H_2SO_4 and boiling for ten minutes in ethyl alcohol. Figures 4; references 10: 3 Russian, 7 Western.

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UDC 538.113:541.67

PARAMAGNETISM OF POLYMERS WITH SYSTEM OF CONJUGATED DOUBLE BONDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 294, No 6, Jun 87
(manuscript received 24 Dec 86) pp 1404-1407

[Article by M. A. Kozhushner, L. S. Lyubchenko and M. I. Cherkashin,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] An analysis of paramagnetic characteristics of polymeric systems has shown that the paramagnetism of a system of conjugated double bonds is due to heterogeneity in the formation of the unordered solid phase. The origins of paramagnetic centers in the system of conjugated double bonds is attributable to structural distortions in the polymer arising from intermolecular reactions. The distortions lead to breakage of π -bonds, i.e., a complete or virtually complete disappearance of energy gaps between the singlet and triplet states. As a result of the deformation the molecule exists in a biradical state. Precipitation of polymer molecules with a system of conjugated double bonds into an amorphous phase leads to a metastable configuration of the molecules. The latter state is due to the long transition times required for formation of the crystalline state. The energetically favored configuration is facilitated by deformations, which lead to the formation of paramagnetic centers due to disruption of the π -bonds. References 15: 12 Russian, 3 Western.

12172/9835

CSO: 1841/428

ADVANCES IN POLYMER LIQUID CRYSTALS

Moscow KHIMICHESKIYE VOLOKNA in Russian No 3, May-Jun 87 pp 4-12

[Article by V. P. Shibayev]

[Abstract] A review is presented of advances in polymer liquid crystals, covering the basic transformations and characteristics. Consideration is given to lyotropic and thermotropic mesomorphisms, followed by a discussion of smectic, nematic, and lyotropic liquid crystals. Rigid and semi-rigid polymers are represented by polyisocyanates and aromatic polyamides, while flexible polymeric chains are represented by the polysiloxanes and polyphosphazenes. The review ends with some applications of polymer liquid crystals, including their use for reinforcement of non-liquid crystal polymers and utilization in composites. Finally, note is made of the fact that the lack of adequate quantities of various reagents hinders basic research on polymer liquid crystals. Figures 10; references 40: 10 Russian, 30 Western.

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CSO: 1841/452

UDC 677.64.6:61

TREATMENT OF CELLULOSE STAPLE FIBERS FOR ANTIMICROBIAL RESISTANCE

Moscow KHIMICHESKIYE VOLOKNA in Russian No 3, May-Jun 87 pp 41-42

[Article by V. I. Shlyakhov, O. I. Pesnya, L. N. Andrianova, and N. G. Shubenkin]

[Abstract] Quaternary ammonium compounds, particularly halides, have been shown to impart to textiles antimicrobial resistance [Klesper, H., Mell. Textilber., Bd. 52 (5): 592-595, 1971]. The studies were presently expanded to assess the efficacy of such compounds in imparting microbial resistance to cellulose staple fibers, using both tetraalkylammonium and alkylpyridinium chlorides and stearates. The activated fibers were tested against pathogenic staphylococcus and E. coli after repeated washings, following saturation and fixation of the compounds on the fibers. The resultant data demonstrated that both class of compounds imparted antibacterial resistance to the fibers. However, fibers treated with the water-soluble chlorides and short-chain stearates (tetramethyl-, tetraethyl-, tetraoctyl-) were found to be suitable only on a single-use basis, rapidly losing their antimicrobial activities. Multiple-use fibers were obtained by treatment with water-insoluble long-chain tetraalkylammonium and alkylpyridinium stearates. Tables 2; references 6: 5 Russian, 1 Western.

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SYNTHESIS OF POLYMER SURFACTANTS BASED ON DERIVATIVES OF NAPHTHALENE AND
FORMALDEHYDE

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 2, Mar-Apr 87
(manuscript received 4 Jun 86) pp 29-32

[Article by M. A. Kuchkarova, M. I. Umarova and U. K. Akhmedov, Institute of
Chemistry, UzSSR Academy of Sciences]

[Abstract] Water-soluble oligomers based on sodium naphthalene-2-sulfonate and formaldehyde were synthesized by polycondensation in an aqueous medium with varying molar ratios of the initial monomers, temperature, reaction times, and pH. The composition of the initial monomer mixture influenced the yield of polycondensate and the reaction rate. The optimal molar ratio of sodium naphthalene-2-sulfonate to formaldehyde was 1:4. Aqueous solutions of the oligomers produced conduct electrical current and decrease the surface tension of water to 52 dyn/cm at a concentration of 1 g/dl. The optimal synthesis temperature was 363 K; reaction time was four hours. The formaldehyde condenses with the sodium naphthalene-2-sulfonate at position three of the aromatic ring. Figures 2; references 3: 2 Russian, 1 Western.

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UDC 539.184:621.378:535.14

LASER-INDUCED REACTION OF Yb ATOMS WITH HYDROGEN CHLORIDE IN GAS PHASE

Moscow KHIMIYA VYSOKIY ENERGII in Russian Vol 21, No 3, May-Jun 87
(manuscript received 13 Feb 86) pp 255-257

[Article by S. K. Borisov, N. A. Karpov, B. B. Krynetskiy, V. A. Mishin, A. M. Prokhorov, and O. M. Stelmakh, Institute of General Physics, USSR Academy of Sciences]

[Abstract] A previous article had shown the possibility in principle of using laser-induced reactions of rare-earth metal atoms for laser separation of isotopes and purification of substances. This article presents the results of a study of the chemical reaction of ytterbium atoms in the 3P_1 state with hydrogen chloride. The reaction of Yb in the 1S_0 state with HCl is endothermic while when Yb is raised to the 3P_1 state (with irradiation by light of wavelength 55.648 nm), the reaction becomes exothermic, allowing us to expect that there is a significant difference between rates of the dark reaction and the reaction with excited atoms. Experiments were performed in a gas flow-through reactor and indicated that the atomic-molecular reaction was indeed initiated in the gas phase. For raising Yb from the 1S_0 to the 3P_1 state, a dye laser, based on rhodamine 110, with a pulse generation range of 5 MHz and a power of 50 mJ was used. The radiation of a second dye laser, based on rhodamine 6Zh, was aimed at the reactor collinearly with the first laser beam at a distance of 5 mm below the gas flow and tuned to the $\Delta V = -2$ transition of the YbCl molecule. When the first laser was tuned to the atomic transition frequency, the laser-initiated luminescence rose to the region generated by the second laser. The luminescence spectrum was identified as that of YbCl, the product of the Yb-HCl reaction. The cross section of the reaction between the excited Yb atoms and HCl is characteristic of harpoon-type reactions, which are the fastest reactions involving neutral atoms. Investigation of laser-induced atomic reactions of rare-earth elements in the gas phase is of interest for isolation of individual elements from multicomponent mixtures and separation of isotopes. On the other hand, the use of flow-through systems allows spatial separation of sequential reactions, important for quenching and isolation of products of selective photochemical reactions. Figures 2; references 7: 3 Russian, 4 Western.

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C80: 1841/416

CURRENT DEVELOPMENTS AND TRENDS IN USE OF IONIZING RADIATION IN BIOTECHNOLOGY:
LITERATURE REVIEW

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 4,
May-Jun 87 pp 8-12

[Article by A. S. Klimentov, All-Union Scientific Research Institute of
Hydrolysis]

[Abstract] A review is presented of current developments and trends in the use of ionizing radiation in biotechnology. Current plans for the 12th Five-Year Plan anticipate that the use of various forms of natural and generated radiation shall increase 1.5- to 2-fold in the USSR. The review covers development of new methods of efficient generation of ionizing radiation and improved utilization of radionuclides. While primary attention was given to the development of radiobiology in medical research, diagnosis, and therapy in the past, considerable attention has been accorded to sterilizing food-stuffs and inducing desirable mutations in plants, animals, and microorganisms more recently. In biotechnology, intensive efforts are being directed toward the use of ionizing radiation in modifying natural products, inducing microbial mutations, and physiologically modifying seeds. References 38 (Russian).

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UDC 546.214 + 535.211

NON-EQUILIBRIUM OZONE BREAKDOWN UNDER ACTION OF PULSED IR-LASER IRRADIATION

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 6, No 4, Apr 87 (manuscript
received 11 Apr 86) pp 455-459

[Article by N. Yu. Mordkovich, B. S. Lunin, V. V. Timofeyev and Yu. N. Zhitnev,
Moscow State University imeni M. V. Lomonosov]

[Abstract] Pulsed laser pyrolysis of ozone-containing mixtures sensitized with SF₆ was carried out under a constant pressure of less than 3 Torr. Under the action of a CO₂-laser, multiphoton excitation of chemically-inert SF₆ molecules took place. As a result of rapid V-T and R-relaxation, gas temperatures of 600-1000 K were reached, showing that the chemical process was strictly of a thermal nature. To permit calculations to be performed, the conditions of pulsed laser pyrolysis were selected so that the conversion rate would not exceed 5%. It was shown that, in the temperature range of 900 to 970 K, ozone breakdown was a non-equilibrium process caused by a combination of vibrational levels normally found below the threshold of dissociation. Thus, using the method of pulsed laser pyrolysis, the lower limit of non-equilibrium ozone breakdown was determined experimentally for the first time at high temperatures. Figures 2; references 17: 9 Russian, 8 Western.

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CSO: 1841/414

DATA BASE OF BIOLOGICALLY ACTIVE COMPOUNDS

Riga NAUKA I TEHNIKA in Russian No 2, Feb 87 p 5

[Article by V. Masin, "The Priznak Expert System"]

[Text] Specialists engaged in searches for new biologically-active chemical compounds (medicines and plant-protection agents) will be able to obtain the most varied consultations if they turn to a query of the expert system "Priznak," developed at the Organic Synthesis Institute at the LaSSR Academy of Sciences.

A data base including information on the structures of chemical compounds and their biological activity is entered in the Priznak system. The Priznak knowledge base contains structural fragments responsible for particular types of biological activity and their statistical evaluation. The new expert system is equipped also with a set of programs which serves to form the knowledge base and to enable it to be used as an "electronic adviser."

By turning to the expert system, the user will be able to obtain not only information on structural fragments (indications of a given activity) and their compounds and answers to compound inquiries, but also a prediction of the most probable biological activities for the substance being synthesized. The Priznak expert system works in a dialogue system, and the chemists use the diagram language of structural formulas, which is natural for them. This new electronic adviser considerably facilitates and accelerates the development of new medicines and plant protection agents.

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COMPUTERIZED CHEMICAL DATA BASE IN YEREVAN

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 29 Apr 87 p 2

[Article by SOTSIALISTICHESKAYA INDUSTRIYA correspondent N. Ordinyan, Yerevan: "An Electronic Encyclopedia"]

[Text] A bank of physicochemical data of substances developed by specialists of the Moscow Chemical Technology Institute imeni D. I. Mendeleyev and the Yerevan Department of the Okta Plastpolimer Scientific Production Association has been put into use at the Yerevan Production Association.

"This enables complex information to be obtained on the physicochemical properties of pure substances encountered in organic synthesis production," says G. Sarkisyan, chief of the computer center. The new, unusual encyclopedia reduces time spent searching for required data and simplifies development and use of automated programs.

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